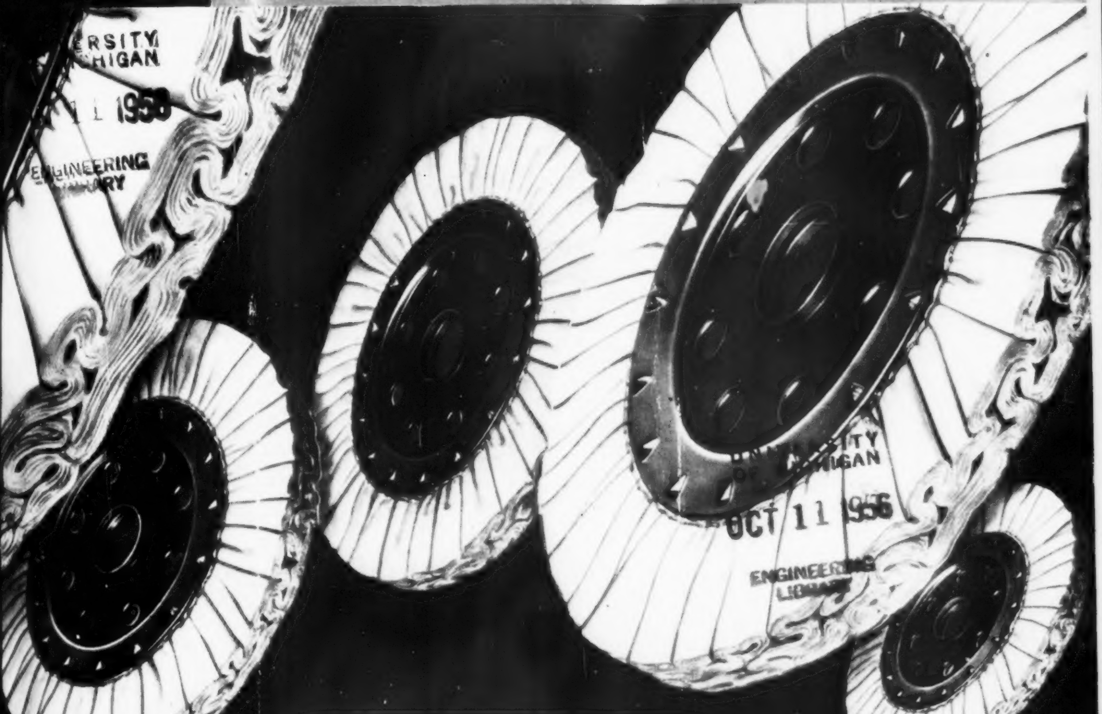
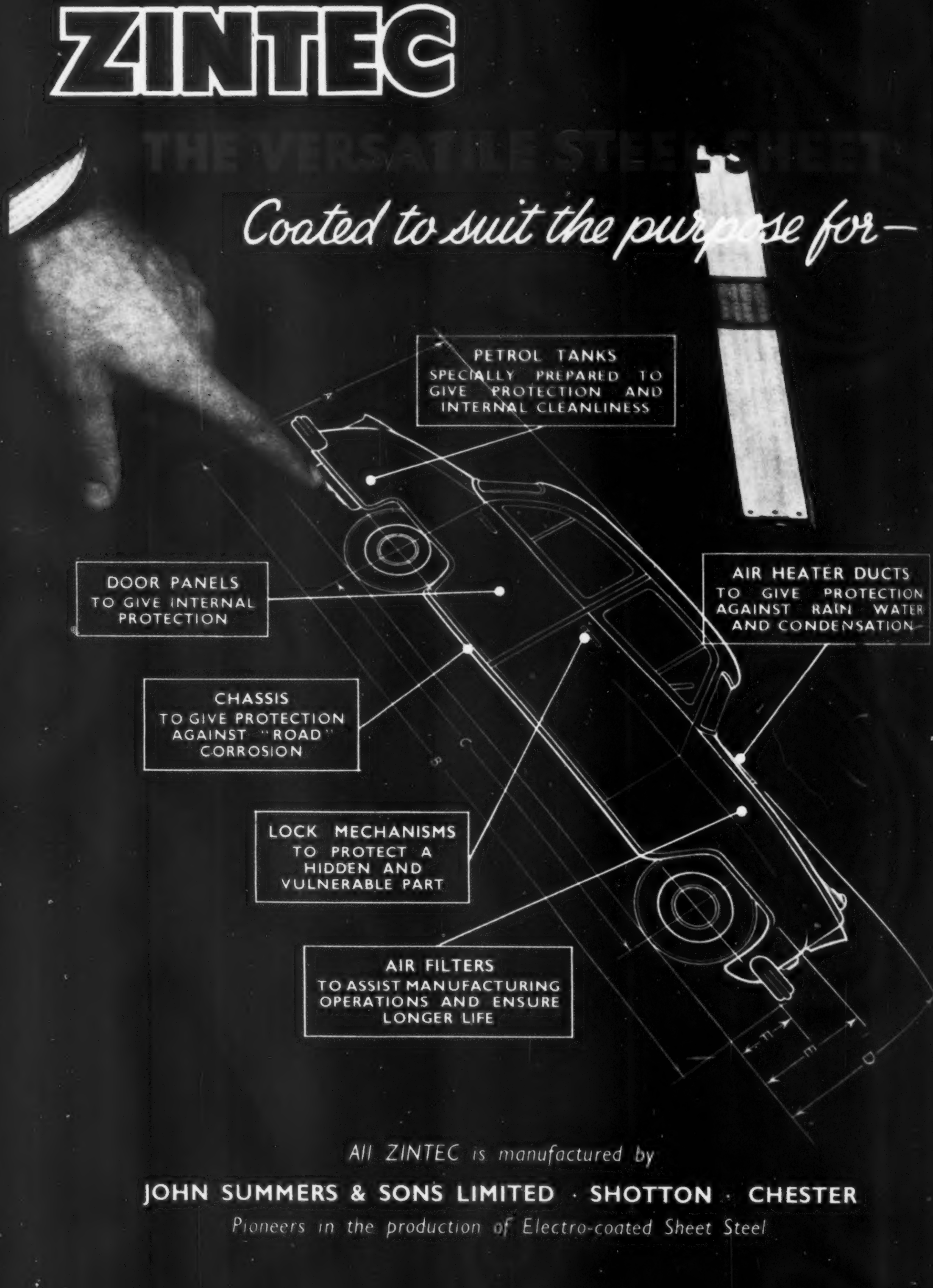
# metal finishing journal

INT APPLICATION, ELECTRODEPOSITION, VITREOUS ENAMELLING,
LVANIZING, METAL SPRAYING and all METAL FINISHING PROCESSES

Vol. 2 No. 21 (new series) SEPTEMBER, 1956




ZINTEC
THE VERSATILE STEEL SHEET
Coated to suit the purpose for—
PETROL TANKS
SPECIALLY PREPARED TO GIVE PROTECTION AND INTERNAL CLEANLINESS
DOOR PANELS
TO GIVE INTERNAL PROTECTION
AIR HEATER DUCTS
TO GIVE PROTECTION AGAINST RAIN WATER AND CONDENSATION
CHASSIS
TO GIVE PROTECTION AGAINST "ROAD" CORROSION
LOCK MECHANISMS
TO PROTECT A HIDDEN AND VULNERABLE PART
AIR FILTERS
TO ASSIST MANUFACTURING OPERATIONS AND ENSURE LONGER LIFE
All ZINTEC is manufactured by
JOHN SUMMERS & SONS LIMITED · SHOTTON · CHESTER
Pioneers in the production of Electro-coated Sheet Steel

# metal finishing journal

September, 1956 — AN INDUSTRIAL NEWSPAPERS PUBLICATION — Vol. 2, No. 21 (New Series)





*Official Organ of the*

**INSTITUTE OF VITREOUS ENAMELLERS**

*President:*
SIR GEORGE BRIGGS

*Chairman:*
W. THOMAS

*Secretary:*
J. D. GARDOM
John Gardom & Co., Ripley, Derby
*Telephone:* Ripley 136

*Published on the 15th day of each month by*

**INDUSTRIAL NEWSPAPERS LIMITED**

*Chairman and Joint Managing Director:*
Barrington Hooper, C.B.E.
*Joint Managing Director and Commercial Director:*
F. Barrington Hooper, B.A.
*Director:*
F. R. Lewis
*Director and Secretary:*
E. G. Weston

**JOHN ADAM HOUSE**
**17-19 JOHN ADAM STREET**
**ADELPHI, LONDON, W.C.2**

*Telephone:* TRAfalgar 6171 (P.B.X.)
*Telegrams:* Zacatecas, Rand, London

*Subscription Terms:*
Home and Overseas 24*s.* per annum prepayable
Single copies 2*s.* (2*s.* 4*d. post free*)


**THIS JOURNAL IS DEVOTED TO THE SCIENCE AND TECHNOLOGY OF PAINT APPLICATION, ELECTRODEPOSITION, VITREOUS ENAMELLING, GALVANIZING, ANODIZING, METAL SPRAYING & ALL METAL FINISHING PROCESSES. THE EDITOR IS PREPARED TO CONSIDER FOR PUBLICATION ANY ARTICLE COMING WITHIN THE PURVIEW OF "METAL FINISHING JOURNAL" AND ALL SUCH ARTICLES ACCEPTED WILL BE PAID FOR AT THE USUAL RATES.**

# Contents

# SHEEP'S CLOTHING

*THE practice of protecting a corrodible metal from environmental influences which could adversely affect its appearance or strength, by depositing on its surface a coating of another metal unaffected by such influences has occasionally been criticised in the past on the grounds that it gave to the object concerned a false semblance of being constructed of the more noble metal, whereas in fact it was only sporting it as an external cover of minimum thickness. No-one today would seriously claim, unless they had happened to fall a recent victim to a glib confidence trick, that an electrodeposited noble coating on an inferior metal amounted to misrepresentation, but there are those, and their numbers do not decrease with the passing years, who press for a greater use of metals inherently resistant to corrosion rather than the adoption of methods of protection which are successful only to varying degrees.*

*The contrary view is also frequently and forcefully put to the effect that it is sounder practice economically to make a component from a material which is in itself inexpensive and in adequate supply, but which may be subject to corrosive attack, and to protect this metal with a layer of another metal which is usually considerably more costly and frequently in short supply. In this way the most effective use is made of scarce and costly materials.*

*The comparative costs of a stainless-steel article and an equivalent article fabricated from mild steel and subsequently plated with nickel and chromium do not at the present time greatly favour the former, although it is argued that the longer life and reduced maintenance requirements which can be expected from the use of stainless steel do offset in some measure the higher initial cost. Nor is stainless steel the only material of a corrosion-resistant nature whose claims are being pressed. In recent months the virtues of chemically or electrolytically polished and anodically coated super-purity aluminium have been loudly sung, and there have been prophets who have foreseen for this material a rapidly expanding use at the expense of nickel-chromium plating.*

*It is perhaps profitable to consider why so many assaults are currently being made on the nickel-chromium plated finish which has held virtually undisputed sway in many fields for many years. In some instances the movement is impelled by the difficulties of obtaining adequate supplies of nickel, but the sponsorship of the use of* 18/8 *stainless steel obviously cannot have this as a motive.*

*The process of nickel-chromium plating has been subject to research and development for some thirty years and it could reasonably be expected that most of the problems associated with its operation had found a satisfactory solution. That this is far from being the case becomes readily apparent on listening to any technical discussion on the subject. Furthermore, the number of users of nickel-chromium plated articles and components in outdoor service who profess themselves to be profoundly dissatisfied with the performance and life of the finish shows little sign of diminishing, and it may well be that an attempt to give greater satisfaction to consumers is the mainspring of the quest for other materials and processes.*

*Although it is true that many individuals and institutions, and hence presumably also metal-finishing processes, are able to thrive in the face of continued criticism, this is not a very safe attitude to adopt. Although traditional habits and capital investment in plant may combine to slow up technical advance a process will only go on being used as long as it continues to fulfil its particular function more effectively than any other.*

*It was the ill fit of the sheepskin which he had donned that led to the downfall of the wolf, and it may well prove that too frequent glimpses of the underlying metal through the silvery fleece of the nickel coating is going to lead to the rejection of the process unless proper action is taken to restore public confidence in its virtues.*

# Talking Points by "PLATELAYER"

TOPICAL COMMENT FROM THE MAIN LINES AND SIDE LINES OF METAL FINISHING

### FROM THE CRADLE

THE METAL-finishing industries play an important part in man's requirements when he first enters this vale of tears—from surgical equipment to safety-pins, cradles, and push-chairs. But at the other end of the journey they are far less prominent. Apart from some types of fittings the field is practically untouched in this country. Not so in the U.S.A., however, where those who have read Evelyn Waugh's satire on the mortician's art will know that the scope is much greater.

We were prompted to these thoughts by seeing a photograph of an American phosphating plant for finishing welded, pressed-steel burial caskets, which are produced on a considerable scale. After phosphating, the caskets are sprayed with metallic pigmented lacquers in various shades of copper, bronze, silver and pastels and then a clear, hot-spray lacquer coat is applied. Finally, the caskets are hand-rubbed and polished to bring out the brilliance of the finish.

Here is a field of enterprise for someone with spare steel-fabricating facilities.

### SOLUTION TO A PROBLEM

AN INTERESTING new development in packaging has arrived which will do much to simplify the handling of some kinds of chemicals. A water-soluble polyvinyl alcohol foil is now available which can be used for packaging fine powders such as wetting agents which are difficult or unpleasant to handle or measure out in small amounts when they are used in various processes. All that is necessary is to throw the complete package into the bath, where it dissolves quickly, thus releasing the active material. It would be as well to check that traces of polyvinyl alcohol do not interfere with the process before introducing the material, however. In the absence of such a check someone might conceivably discover a new bright plating process!

### EXHIBITIONISM

ONE OF THE features of our age is the continual increase in the number of industrial exhibitions. There is, from time to time, even some expression of doubt as to whether there are not altogether too many of them, although, of course in limited numbers they can be very useful indeed.

In some instances firms feel that they have to exhibit because their competitors are also exhibiting, a position which would not arise if the exhibitions were not held at all.

Evidently, however, in France they are taking the view that the demand for exhibition space is going to continue. A vast new exhibition building is being constructed outside Paris, having a floor space of nearly one million sq. ft. It is expected to be finished in 1958. The building will be triangular in shape, for some reason which is not very clear. One thing is certain, however, the mere fact that the building exists will be a powerful incentive in itself towards keeping it fully occupied.

### TAKING IN WASHING

AN INTERESTING example of a low cost service operating at a high efficiency is provided by a company which has a service hiring cleaning cloths to industry at a cost much cheaper than that involved in buying rags.

When the dirty cloths are received back by the suppliers, the oil is extracted from them and used for firing the boilers used for the laundering plant. It is not stated whether the swarf removed from the cloths is also melted down!

### TERMINOLOGICAL INEXACTITUDES

MANY words have technical meanings which diverge widely from those in accepted common usage, but when it comes to turning the simplest words into something quite different, the financial writers are the most adept. Recently, we were somewhat disturbed to read that most metals had weakened considerably during the previous few days; there was some compensation, however, in that textiles were stronger. On the other hand, oils were heavy, but it was only when we learned that copper was buoyant that we realised the gravity of the situation!

Some of our metallurgical terms would likewise cause confusion in other circles. In fact, nowadays, the meanings of some words or terms depend entirely on where one reads them. An account of plants for pickling in a cookery book would read very differently from one on the same subject in a text-book on steel-making. One could imagine that a study of the meanings of the same phrases in different branches of technology, and their etymological derivation would be fascinating—and probably amusing.

I should be interested to hear of striking examples of such different uses of phrases from readers, and will endeavour to publish some of the more unusual ones.

# BRIGHT NICKEL PLATING

## An Account of its Early History, Evolution and Development

by Dr. I. R. BELLOBONO*

THE electroplating industry and its use of nickel have grown with remarkable rapidity in recent years. It is estimated that the consumption of nickel constitutes 75 per cent. of the metal absorbed by the electroplating industry. Actually, this amounts to 18 per cent. of the world production of nickel of which it is the third largest consumer with 18,000 tons per annum, only coming after its use in the alloy steels and alloys containing high percentages of nickel, like Monel, Inconel and Nimonic.

It thus seems opportune to give an account, if only in broad outline, of the prodigious development of the nickel-plating industry from its vague early gropings to its organized techniques of today with their greater degree of scientific maturity.

Experimental electrodeposition followed very shortly after the discovery of electric current, when in 1800 Nicholson and Carlisle decomposed water into hydrogen and oxygen and Cruikson deposited, on an electrode, copper from a metallic solution. Even before the studies of Cruikson, which were carried out in London with a Volta electric motor, some few months after the discovery of the Volta cell in 1800, Brugnatelli, a collaborator of the great scientist from Como, at Pavia, was already effecting electrodepositions of metals, *viz.*—silver, zinc, mercury, copper. Of the various experiments made by Brugnatelli at the beginning of the 19th century, may be mentioned those in which he electrodeposited gold, and his attempts at preparing alloys by means of electric current, indisputable documentary evidence of which still remains. Perhaps the form in which he expressed himself, which savoured rather too much of alchemy, did little to make him famous among his contemporaries, who by this time had become accustomed to more scientific forms of expression. This, however, should not affect the claim that electroplating had its birth in Italy. And not its birth alone, for after Brugnatelli there are other names worthy to be remembered—Nobili([1]) the discoverer of metallic chromium and, towards the middle of the 19th century, Zantedeschi([2]) and Marianini([3]).

** Based on a series of articles published by the Italian journal Galvanotecnica. This English version is reproduced with the collaboration of the editor and the author of the work.*

### Nickel Plating

The first strictly electro-metallurgical patent was granted to James Short, of Birmingham, in 1810, for coating "cast iron, lead and copper with copper or nickel" by means of what the pioneers called "galvanic current".

Electrodeposition has, as has already been noted, the specific property of modifying the surface properties both of metals and non-metals. Its resultant benefits include not only an aesthetically improved appearance, but also increased hardness and resistance to chemical or atmospheric corrosion. The first commercial coating of nickel seems to have been made in Boston by Isaac Adams in 1865, with a bath containing 75 gm. of nickel-ammonium sulphate per litre of water. A solution of this sort, however, which in those early days was used almost exclusively, had certain defects. Worst of all, its content of nickel was small and it had a low conductivity. It provided deposits of sufficient hardness, however, for contemporary needs.

The next development from an electrolyte of this sort, which could well be described as the foundation stone of the story of nickel-plating, was in 1878, when Edward Wiston introduced boric acid. This innovation was made empirically. It was not known that the true significance of this addition was its function as a buffer, as was found subsequently; that is to say, it had the function of neutralizing the alkali produced as a consequence of the low cathode efficiency.

With the advent later of chromium-plating on nickel, it was found that nickel deposited in this manner was not very good as an undercoat; it tended, in fact, to adhere very imperfectly to the overlaid chromium. The double sulphate eventually became almost entirely obsolete, although some improvements were tried with it, such as additions of ammonia and sodium sulphite which enabled higher throwing power to be obtained as well as adequate adhesion of the deposits, especially on brass and zinc. Even today, some similar baths are still in use for electrotype printing or for thin deposits of semi-bright nickel of a silver-brass tint. In general, however, the double sulphate is no longer used for such purposes and, as a result

of the researches of Watts between 1916 and 1925, the baths bearing his name became standard in this field of activity.

Two solutions were available, the first, termed "light", for general and current use contained:—

| | |
|---|---|
| nickel sulphate ... | 150 gm. per litre |
| boric acid ... ... | 10 gm. per litre |
| sodium chloride ... | 6 gm. per litre |

The second solution, termed "heavy", for making deposits more rapidly by using higher current densities contained:—

| | |
|---|---|
| nickel sulphate ... | 300 gm. per litre |
| nickel chloride ... ... | 20 ,, ,, ,, |
| boric acid ... ... | 12 ,, ,, ,, |

The chlorides were present in order to accelerate the corrosion of the anode.

Deposition of nickel was followed by the deposition of chromium. First, however, it was necessary to wash the specimen, dry it, polish and brighten it mechanically. In this series of operations about 30 per cent. of the plated metal was lost. Then a degreasing treatment was needed for the surface to be suitable for receiving its deposit of chromium. This soon led to the development of solutions from which bright deposits could be obtained directly by electrolysis.

### Bright Nickel Plating

The first observations made regarding the action of colloids, particularly gelatine[4], on electrolytic deposits appeared in 1886 and the development of research in this field was stimulated above all by the Betts[5] process (1905) for the electrolytic refining of lead. This author had perceived that some salts of lead could give compact deposits of metal if the electrolyte contained a proportion—quite a small proportion, indeed—of glues, gelatines or gums.

But it was 1920 to 1930 which was the period in which there was the prime impulse to make use of nickel baths. This was the decade of rapid nickel-plating.

In 1920 Todd and King patented "mirror-bright" nickel as the result of using tragacanth gum. Hoefer[6] led in 1931 a discussion of the marked effects which small amounts of addition agents exercise in refining the grain-size of the deposited metal and the consequent compactness and brightness of the deposit itself. The deposit could thus still be of a certain thickness, although it had already been noted that when highly polished specimens were plated for a short time in an ordinary nickel solution, they did come out bright: but the coated layer was too thin for most applications.

The first process for bright nickel which received more favourable attention was that patented by Schlotter[7] in 1932, which involved addition to an ordinary Watts bath of sodium naphthalene trisulphonate in concentrations of approximately 35 grams per litre, with operation at a potential of 4 to 5½ volts and at a temperature of 45 to 55° C. Schlotter baths enable thicker deposits to be obtained than those obtainable by adding so-called Paal mixtures (based on citric or tartaric acids) but it was necessary to operate them at a rather low current density, which could not be raised by adding chlorides as this led to clouding of the deposit.

Meanwhile, the development of methods for the measurement of *p*H, led to studies of the influence of acidity in nickel-plating baths. Madsen, in 1924, patented the use of hydrogen peroxide as an anti-pitting agent. Pitting, due to the partial evolution of hydrogen at the cathode, owing to low cathode efficiency, became significant in extent at too low a *p*H.

The advent of bright nickel and its special baths gave rise to the introduction of surface-active or wetting agents, but full development of these last only occurred subsequently[8]. These agents cannot be employed in baths which are agitated by air, because for the most part, they have high foaming power.

From 1937, the number of patents for additions to the traditional baths of particular substances suitable for causing the deposited metal to be "bright" multiplied greatly. Of these, for historical reasons, may be recorded those in 1938 of Gustav Soderberg[9], a name well-known in the field of applied electrochemistry, as well as those of Puri and Juncja[10] for inorganic colloids of the type of selenium or of the hydroxides of aluminium and iron—to quote merely a few of those which were first introduced. Inorganic addition agents were utilized by Lapin and Matwejew[11], whose Watts-type bath contained 0·08 grams per litre of cadmium sulphate. In this connexion it is noteworthy that Raub and Wittum[12] observed that cadmium in quantity is rather harmful.

There were then developed baths with mixed inorganic and organic brighteners, *e.g.*, those of E. Baker put up by the Houdaille-Hershey Corp., containing 0·05-0·5 grams per litre of lead in the form of salts and enough sodium formate to retain the lead in solution; those of Parker-Wolverine[14], who coupled the action of traces of zinc and mercury salts with that of sodium naphthalene disulphonate; those of Udylite[15] who add phenyl-arsenic acid (1-2 gm. per litre) as well as 0·1-0·2 gm. per litre of cadmium, zinc, selenium or tellurium or, in more recent years[16], salts of thallium in combination with aryl sulphonates or sulphinates.

A. Wesley and J. Carey[17] obtained for the International Nickel Co. in 1942 a patent for semi-bright nickel, more or less similar to that obtained by R. Tuttle for the Deutsche Gold u. Silber Scheideanstalt ("DEGUSSA") in 1938 and har-

monizing, above everything else, the concentration of boric acid with the current density at which the solution operated. Large amounts of boric acid with a relatively high current flow diminish the throwing power of the bath and the hardness of the deposit.

The bath of the Harshaw Chemical Co.([18]) comprised in 1937, selenium dioxide as inorganic brightener (approximately 0·06 gm. per litre), which deposited with the nickel to the extent of 0·3-0·5 per cent. together with naphthalene disulphonic acid (6·2 gm. per litre) and 0·06 gm. per litre of lauryl sulphonate as anti-pitters. As organic brighteners they also started to use—besides sulphonates—sulphonamides and sulphonimides([19])

The following is a typical example([20]):—

| | |
|---|---|
| $NiSO_4 \cdot 7H_2O$ ... ... | 240 gm. per litre |
| $NiCl_2 \cdot 6H_2O$ ... ... | 37·5 „ „ „ |
| $H_3BO_3$ ... ... ... | 37·5 „ „ „ |
| $2{\cdot}2^1{-}44^1$ tetramino-$5{\cdot}5^1$ dimethyl-diphenyl methane sulphate ... | 0·01 „ „ „ |
| Sodium salts of saccharine | 1·0 „ „ „ |
| sodium lauryl sulphonate | 0·25 „ „ „ |

$pH = 3{\cdot}0\text{-}4{\cdot}5$

Bath at 45-55° C

Current density 3·3-4·4 amps per sq. dm.

Toluol or toluidine sulphonates were used, instead, in the bright nickel plating bath of the McGuan Chemical Co.([21]). It was found (*see* above) that the addition of zinc or cadmium in concentrations of 0·2-0·3 grams per litre to the usual Watts baths gives a homogeneous and sufficiently bright deposit([22]). From this stemmed other patents of the Udylite Corp.([23]), which made use at the same time of 1-2 gm. per litre of saccharine, of 0·5-1·0 gm. per litre of *p*-sulphondichloramide and of 1 gm. per litre (to get saturation) of *o*-, *m*- and *p*-toluenesulphonamide.

To the Seymour Manufacturing Co.([24]) is due the development of the following bath:—

| | |
|---|---|
| $NiSO_4 \cdot 7H_2O$ ... ... | 231 gm. per litre |
| $NiCl_2 \cdot 6H_2O$ ... ... | 50 „ „ „ |
| $H_3BO_3$ | |
| *o*-sulpho-benzaldehyde at 43-49° C ... ... | 3·12 „ „ „ |

The Dupont De Nemours Co.([25]) obtained in 1941 a bath of the greatest brightening power by adding 0·1 gm. per litre of a sulphurated protein material and of *o-m*-sulphobenzaldehyde.

Udylite([26]) now have a 1948 patent covering the addition of unsaturated compounds of the chlorovinyl acid or bromo-vinyl-sulphonic acid type (over 1 gm. per litre) as brighteners.

On the subject of these unsaturated organic compounds, it may be recalled as a scientific curiosity, the fact that the first electroplaters to produce bright nickel-plating added to their baths an extract of onions. They presumably owed their unexpected good fortune as empirical investigators to the allyl isosulpho-cyanides contained in this extract.

Bright nickel-plating baths with a content of cobalt made their appearance with L. Weisberg([27]) in 1938.

Apart from the cost of the cobalt—owing to the relatively high content of it in the deposits of nickel (about 12 per cent. at 2·8 amps per sq. dm.) —there was a drawback in the presence of formaldehyde, which had to be added for depolarization and was the cause of considerable bodily discomfort. With these baths, however, success was achieved in obtaining good brightness and pitting was able to be reduced to a minimum.

Subsequent improvements have been incorporated. A start was made by replacing the formaldehyde with sodium formate([28]), then by reducing the content of cobalt in the baths and, more important than anything else, by reducing it in the anodes from 18 to 5 per cent. and, finally, to 1 per cent.([29]). In spite of this there have not been wide applications, perhaps on account of poor levelling power ([30],[31]). There have been, however, several formulae (among which mention may be made of those of Bosel Maletra Société Industrielle de Produits Chimiques([32]), in which there are added to 47 gm. per litre of $CoSO_4$ and 190 gm. per litre of $NiSO_4$ some 2 gm. per litre of NaCl, 5 gm. per litre of KBr and 3 gm. per litre of $Na_2SO_4$. There were obtained in this way deposits of 50 per cent. nickel and 50 per cent. cobalt with a Brinell hardness of 300-400.

Young and Eberman ([33]) added gelatine to a bath which operated with 135 gm. per litre of $NiSO_4 \cdot 6H_2O$, 35 gm. per litre of $CoSO_4 \cdot 7H_2O$, with a *p*H of 2·0-3·0 at a current density of 5·5 amps per sq. dm.

In Italy, meanwhile, rapid bright nickel-plating ("rapid" because it is only with these particular brighteners that a deposit is obtained reasonably quickly, while with the original gums and gelatines a bright deposit was obtained, only extremely slowly) was first established in April, 1948, with the work of Prof. Eugenio Bertorelle([34]). He, with the material aid of Baratini and Co., builders of plating plants at Milan, developed a bath on the basis of nickel sulphate, nickel chloride and boric acid, using bicyclic and aliphatic organic compounds as brighteners.

Air-agitation near the cathodes has been applied with a view to avoiding most of the phenomena of concentration polarization which give rise to "crude" deposits and to avoiding, in particular, occlusions of hydrogen which are the causes of pitting.

From 1949 onwards the number of patents has increased in a steading rising rhythm, and these have been accompanied by a multiplicity of attempts

at explaining what cathodic factors are conducive to bright deposits. A complete catalogue of them would, in view of their number, be almost impossible to compile([35]) and all that will be attempted here is a review, to the extent that this can reasonably be made, of the most important and widely known of these patents.

Harshaw had already made technical use for the first time in 1941([36]) of basic alkaloid dyes prepared from plants and of certain colouring matters from the amino-anthroquinone group. Only in the last five years, however, has their use been finally developed and perfected.

A systematic study of the properties of surface-active agents was made by Davis, Wolfe and France([37]), with particular reference to Igepon T ($C_{17}H_{13}$-CO-NH-$CH_2$-$CH_2$-$SO_3$Na), to Lyofix D.E., to Saframina KWC, to Nekal BX, to 1-4 isopropyl-naphthalene-sulphonic acid, to cetyl pyridine bromide and to citronellal.

Weaker bath agents belong to the class of *ortho*-nitrotoluol, of *meta*-toluol-aldehyde and pyrrole.

Udylite patented in 1950([38]), a bath containing an acid solution with one or more nickel salts and a small proportion of unsaturated $\alpha$ and $\beta$ sulphonic acids, of sulphonamides and sulphonimides together with even smaller quantities of aldehydes or aromatic ketones or soluble olefine compounds. One of the principal baths consists of:—

| | |
|---|---|
| $NiSO_4 \cdot 7H_2O$ ... | 200-300 gm. per litre |
| $NiCl_2 \cdot 6H_2O$ ... | 30-75 ,, ,, ,, |
| $H_2SO_3$ ... ... | 30-40 ,, ,, ,, |
| Allyl sulphonic acid (salts of Na, K or Ni) | 1-3 ,, ,, ,, |
| Formaldehyde ... | 0·3-0·8 ,, ,, ,, |
| $\alpha$ and $\beta$ tri-chlor-butyraldehyde hydrate | 0·2-0·5 ,, ,, ,, |
| *p*H ... ... ... | 3-5 ,, ,, ,, |
| Temperature ... ... | 40-50° C |
| Current Density ... | 1-6 amps per sq. dm. |

However, the same firm, Udylite([39]), is credited (1950) with a patent, the features of which summarize the claims of preceding patents. It will be useful, therefore, to discuss this patent at greater length with a view to clarifying better the long road travelled up to this point. The object of obtaining ductile and bright coatings is attained by using soluble organic compounds containing the aldehydic or ketonic carbonyl and/or the double olefinic bond.

While the $\alpha$ or $\beta$ unsaturated sulphonic acids like, for example, vinyl or allyl sulphonic acid, give bright coatings on polished surfaces, the rate of brightening of a matt surface is rather low or, rather, they do not rapidly improve the brightness of the original surface. If, however, one adds, for example, chloral hydrate, acetaldol or a mono- di- or tri- allyl amine in amounts varying between 0·05 and 0·15 gm. per litre, there is then soon produced a distinct and notable improvement, especially in the zone of relatively low current density.

The vinyl-allyl-sulphonic acids are excellent in respect of their capacity for maintaining the zones of low current density bright and adherent in spite of the presence of a perceptible amount of zinc as an impurity.

Excessively high concentrations cause brittleness in some cases. The baths can also even contain an amount as high as 75-100 gm. per litre of $CoCl_2 \cdot 6H_2O$ (or its equivalent as sulphate). Baths with nickel sulphamate or nickel fluoborate can also be employed.

The best *p*H values are between 3 and 5. Too low a *p*H (2·0-2·5) tends to slow down the rate of brightening. It is not possible to employ heating coils of lead, or lead-lined tanks, when using baths having a high chloride content (and low sulphate content) owing to lead being easily soluble in such baths.

Still in 1950, Freed and Stocker (per the Seymour Co.([40])) put in a claim for protection for a brightening agent formed from an aryl-aldehyde sulphonate and a reaction product from the action of sulphuric acid with an alykl-substituted mercapto-di-hydro-pyrimidine.

The Udylite Co. now created new baths with aldehydes, unsaturated ketones, with or without chromophoric groups and with aromatic sulpho-acids([41]) and baths containing, besides the other constitutents, salts of thallium([42]), while the E. I. Du Pont de Nemours Co. ([43]) introduced into their baths mainly 1·5 gm. per litre of methyl naphthalene sulphonate.

The 2-7 naphthalene-disulphonates of sodium or potassium in concentrations of the order of 3 to 4 gm. per litre have been studied in the nickel baths of Zdryavtsev, Korol'kova and Fedurkin([44]). These writers operated without agitating their baths at low current densities (0·1-2 amps per sq. dm.) and with agitation when working with a higher range of current densities (1·5 to 5 amps per $dm^2$). Brittle deposits were obtained only when the thicknesses obtained were greater than 25-30 microns.

Between 1948 and 1950 investigations were completed which had been based on the "reverse electro-clearing" principle (electrolytic polishing obtained by alternating the current from one pole to the other) of Nixon and Olsen([45]), applying it to electrodeposition. Periodically reversing the current with the Jernstedt "PR" process, rapid and bright coatings were obtained—particularly of nickel([46]).

Finally, quite recently, other Udylite patents have sought protection([47]) for adding to the bath

of nickel of 0·001-0·002 grams per litre of C-substituted halides of N-alkyl-pyridine, quinoline or iso-quinoline, alternatively of 0·001 gm. per litre of C-substituted quinoline or iso-quinoline and 0·1-0·3 gm. per litre of alkyl or aryl sulphonamides or sulphonates of nickel, alternatively([48]) of 0·1-1·0 gm. per litre of carboxyalkyl halides of pyridine and 0·001-0·005 gm. litre of a compound of di-pyridyl: this jointly with 0·5 to 7 gm. per litre of a cyclic sulphonic acid or of a sulphonamide, alternatively([49]) of an aryl sulphinate (from 0·005 gm. per litre to saturation), like benzene or toluene sulphinate in baths of mixtures of the fluoborates of nickel and potassium. These patents protect, besides, the addition([50]) to a bath of conventional type of the following compounds: a pyrazole N-alkyl (from 1 to 6 atoms carbon) pyridine or quinoline (0·001 to 0·02 gm. per litre) and benzene sulphonamide, sulphonimide, benzene-sulphonic or naphthalene-sulphonic acid (from 0·02 gm. per litre to saturation).

One specific bath described consists of:—

| | |
|---|---|
| $NiSO_4 \cdot 6H_2O$ ... | 200-300 gm. per litre |
| $NiCl_2 \cdot 6H_2O$ ... | 125-145 „ „ „ |
| $H_3BO_3$ ... ... | 40 „ „ „ |
| *o*-benzoyl-sulphinimide | 1-2 „ „ „ |
| *p*-toluene sulphonamide | 1 „ „ „ |
| N-methyl-acetate 4 nitro-5 (-3° pyridine) pyrazol chloride ... | 0·002-0·006 gm. per litre |

This bath operates at 40-50° C with *p*H value 3-5.

The Harshaw patents include([51]): the addition of 0·05-0·5 gm. per litre of coumarin to fluoborate or sulphamate baths. The coumarin in these can be in the simple state or substituted by alkyl or acyl groups containing not more than 4 atoms of carbon. The *p*H is maintained between 2·5 and 5. Other people make use of brighteners consisting of aromatic compounds containing the $C\text{-}SO_2$ group as the most important constituent([52]) or of amino-polyalkyl substances([53]) with a molecular weight of over 100 and of a sulphonic acid derivative with an aromatic nucleus.

Bright and ductile electro-deposits are thus obtained from a fluoborate nickel bath and small amounts of sulphurated quinidine or benzoic sulphonimides([54]).

In this connexion it may be recalled that the fluoborate nickel bath (75 gm. per litre) at 54° C and using 10 amps per sq. dm. was introduced in 1950 by Roehl and Wesley([55]). This bath has the advantage of being able to work with a high current density, but obtains bright deposits by means of judicious additions of brighteners.

Young([56]) adopted, instead, the phosphate bath at temperatures between 25 and 85° C and used current densities between 2 and 12 amps per sq. dm. The electrolyte is prepared by dissolving nickel carbonate or trivalent nickel oxide ($Ni_2O_3$) at 105° C in phosphoric acid (density 1·379) with subsequent addition of alkaline phosphates which allow higher current densities to be used.

A bright and very ductile nickel coating is obtained from a bath developed by International Kenmore([57]), having a base mainly of hydrofluoric and boric acids and brighteners. The HF forms with the Ni a complex fluoride and guarantees a *p*H of between 1 and 6.

The bath contains at least 30 gm. per litre of metallic nickel. There are for preference present as brighteners, a mixture of *para*-toluene-sulphonamide, saccharine and fuchsine.

Also, unsaturated polyvalent (usually tertiary) alcohols, like dimethyl-acetylene-carbinol, have been successfully employed experimentally as agents for obtaining bright nickel when quantities between 0·1 and 1 gm. per litre are used([58]), and in the field of reducible dyestuffs zinc powder and hydrochloric acid have been tried in the presence of sodium bishulphite or hydrosulphite. In addition to fuchsine, which has already been mentioned, use has been made of *para*-rosaniline, methyl violet, aniline blue, aurine and similar substances ([59]).

Semi-bright deposits of nickel have been obtained by W. Canning and Co. Ltd.([60]) from a commercial bath containing 120-140 gm. per litre nickel sulphate, 15-60 gm. per litre nickel chloride, 5-30 gm. per litre formic acid, 30-40 gm. per litre boric acid and 1 gm. per litre coumarin. A *p*H between 2·1 and 2·5 was used. The bath could also contain 0·5 gm. per litre formaldehyde and up to 150 gm. per litre magnesium sulphate. It is operated for preference at 60-80° C and with a current density of 4-6 amps per sq. dm.

Among the baths most recently put into operation, may be mentioned that of United Chromium Inc.([61]), which makes use of a primary brightener of the indazole type (0·005 to 0·05 gm. per litre) and of a secondary (subsidiary) brightener of the aryl sulphonate type. Note should also be taken of the solution of Wagner Bros. Inc., who prefer to add 0·01-1 per cent. of *iso*-thiourea-propionic acid([62]).

Sodium carboxy-methyl cellulose is used as a brightening agent in electro-plating, either nickel or cadmium. One particular patented bath([63]) contains sodium cyanide and 0·05 to 0·1 per cent. of the brightener.

R. Blasberg([64]) introduces enzymes or ferments into a bright nickel-plating bath of the Watts type in order to improve its action.

A bath recently developed by Harshaw([65]), enables the addition to be made of thio-phenol-sulphonic acid (0·15 gm. per litre). in the form of its nickel or cobalt derivatives, in combination with ethylene cyanohydrin (0·3 gm. per litre) and aromatic nitriles or sulphonates. With this bath

*Continued in page 316*)

# MEASUREMENT OF GLOSS in Vitreous Enamels

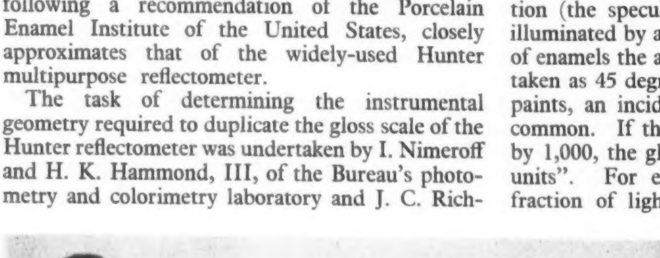
## New Method Developed by U.S. Bureau of Standards

A SIGNIFICANT improvement in the stability and consistency of specular gloss measurements is made possible by a standardized method recently developed at the U.S. National Bureau of Standards. Intended primarily for application to porcelain enamels, the method has established sizes and tolerances for the critical geometric dimensions of specular glossmeters. The resulting gloss scale, following a recommendation of the Porcelain Enamel Institute of the United States, closely approximates that of the widely-used Hunter multipurpose reflectometer.

The task of determining the instrumental geometry required to duplicate the gloss scale of the Hunter reflectometer was undertaken by I. Nimeroff and H. K. Hammond, III, of the Bureau's photometry and colorimetry laboratory and J. C. Richmond and J. R. Crandall of the enamelled-metals laboratory. On the basis of their work, gloss tests for porcelain enamels have been included in the methods recommended by the P.E.I. and the American Society for Testing Materials.

Gloss measurement in the past has been used principally to evaluate the resistance of high-gloss enamels to abrasion or chemical attack. Usually specimens are measured, before and after attack, on the same instrument in the same laboratory. The data thus obtained are useful for determining relative resistance to attack even though a standardized gloss scale is not used. Serious difficulties arise, however, when an attempt is made to compare readings of non-standard glossmeters in different laboratories. A further impulse towards standardization has come in the last few years from the development of porcelain enamels in a wide range of gloss. These enamels make heavy demands on uniformity of product and matching of components made in different plants.

Specular gloss may be defined as the fraction of light flux reflected in the direction of mirror reflection (the specular direction) when the sample is illuminated by a parallel beam of light. In the case of enamels the angle of incidence (and reflection) is taken as 45 degrees. When measuring the gloss of paints, an incidence angle of 60 degrees is more common. If the fraction mentioned is multiplied by 1,000, the gloss is given in conventional "gloss units". For enamels the specular gloss is the fraction of light energy, in parts per thousand,



*Goniophotometer used by the U.S. National Bureau of Standards in standardization of glossmeters for measuring specular gloss of porcelain enamels and other ceramic materials. The purpose was to determine the sizes and tolerances of glossmeter source and receptor apertures which most nearly duplicate the gloss scale of the Hunter multipurpose reflectometer. Previous studies showed these dimensions to be crucial for the duplicability of glossmeter readings. Light from within aluminium box near operator's hand goes through a rectangular window, is collimated, strikes the specimen (held vertically in frame at centre of picture) and is reflected into the receptor arm at right. There the light is again collimated and goes through another rectangular window into the spherical integrating enclosure at extreme right of receptor arm. Angles of incidence and reflection, both of which could be varied, were fixed at 45° for this study. The operator is holding the removable brass plate containing the adjustable source window. The receptor window (not visible) is similarly adjustable in size. The e m f. of three series-connected photocells in the integrating enclosure is measured by the galvanometer and slidewire potentiometer at lower left.*

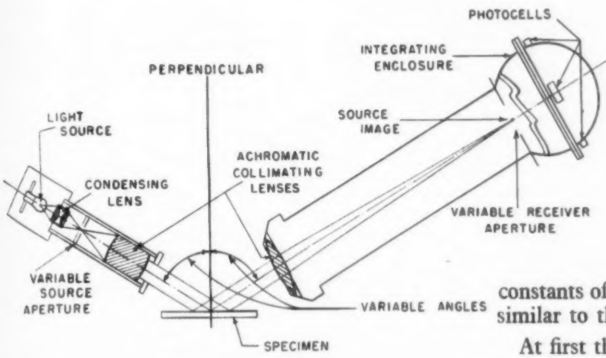



*Diagram showing essential components of the U.S. National Bureau of Standards' goniophotometer used in standardizing specular gloss measurements of porcelain enamels.*

reflected at 45 degrees when the specimen is illuminated at 45 degrees.

Unfortunately, strictly parallel beams are not obtainable, nor can the light reflected in the specular direction be perfectly separated from that in adjacent directions. The Bureau's present studies have shown that disregard of the effects of angular spread among the incident rays (aperture of the source) and among the reflected rays (aperture of the receptor) is largely responsible for the discrepant result obtained with different glossmeters.

In practical glossmeters a beam of light issues from a source, falls on the specimen, and is reflected through a rectangular window into a receptor where its intensity is measured either photoelectrically or in some other manner. The source is oriented with its long dimension perpendicular to the plane of measurement, that is, the plane determined by a ray from the centre of the source and the normal to the specimen at the point of incidence. Since the source is rectangular, the spread of light in the beam will vary in different planes through the optical axis. In this case it is customary to define the "aperture of the source" as the *pair* of angles that measure the spread in the planes perpendicular and parallel, respectively, to the plane of measurement. The long dimension of the receptor window is oriented like that of the source, and the "aperture of the receptor" is similarly defined as a pair of angles.

When the Bureau, acting on a proposal of the P.E.I. Quality Development Committee, took up the problem of glossmeter standardization, an instrument devised at the Bureau in 1936, the Hunter multipurpose reflectometer, was already in wide use and provided a convenient scale of values. Although sufficiently accurate for relative measurements on a single instrument, the glossmeter section of the Hunter reflectometer was designed before the importance of accurate control of field angle was appreciated. In general, therefore, its readings vary from one instrument to another. The problem then was to determine the geometric constants of a glossmeter that would provide a scale similar to that of the Hunter instrument.

At first the possibility was considered of making a direct measurement of the geometry of a Hunter instrument. However, the complexity of the Hunter optical system made such a determination unfeasible. Instead, a special goniophotometer was used as a glossmeter, and its source and receiver apertures were adjusted by trial to duplicate the desired scale and thus to establish the geometry requirements.

The goniophotometer used had been constructed for earlier studies. It is basically a device for throwing a beam of light on to a specimen at any desired angle of incidence and for measuring the light reflected in any direction in the plane of measurement. Light is provided by a standard headlight bulb. Its filament is brought to a focus in the plane of the source window, which thus becomes the effective source. Light from the window is collimated by an achromatic lens before falling on the specimen. The reflected light goes through another achromatic collimating lens which, if the specimen had a mirror surface, would form an image of the source in the receptor window. Then the light enters an integrating sphere in which three phototubes, connected in series, measure the total flux through the receptor window.

Since space conservation was not a problem, the instrument was made sufficiently large to permit measurement of its components with high geometric accuracy. It is so constructed that one can control accurately and independently (1) both dimensions of the rectangular source and receptor windows; (2) angles of illumination and view; (3) beam collimation; and (4) position of source image relative to the receptor window.

One of the Bureau's Hunter instruments was chosen for comparative study. With it the gloss of nearly one hundred specimens was measured. The instrument was set up in the usual manner with the gloss opening in a horizontal position and a sample of appropriate reflectance in position to furnish the comparison beam. The gloss scale was adjusted for linearity by inserting calibrated neutral filters in the gloss beam in front of the receiver window.

Two fundamental considerations guided the

at explaining what cathodic factors are conducive to bright deposits. A complete catalogue of them would, in view of their number, be almost impossible to compile[35] and all that will be attempted here is a review, to the extent that this can reasonably be made, of the most important and widely known of these patents.

Harshaw had already made technical use for the first time in 1941[36] of basic alkaloid dyes prepared from plants and of certain colouring matters from the amino-anthroquinone group. Only in the last five years, however, has their use been finally developed and perfected.

A systematic study of the properties of surface-active agents was made by Davis, Wolfe and France[37], with particular reference to Igepon T ($C_{17}H_{13}$-CO-NH-$CH_2$-$CH_2$-$SO_3Na$), to Lyofix D.E., to Saframina KWC, to Nekal BX, to 1-4 isopropyl-naphthalene-sulphonic acid, to cetyl pyridine bromide and to citronellal.

Weaker bath agents belong to the class of *ortho*-nitrotoluol, of *meta*-toluol-aldehyde and pyrrole.

Udylite patented in 1950[38], a bath containing an acid solution with one or more nickel salts and a small proportion of unsaturated $\alpha$ and $\beta$ sulphonic acids, of sulphonamides and sulphonimides together with even smaller quantities of aldehydes or aromatic ketones or soluble olefine compounds. One of the principal baths consists of:—

| | | |
|---|---|---|
| $NiSO_4 \cdot 7H_2O$ | ... | 200-300 gm. per litre |
| $NiCl_2 \cdot 6H_2O$ | ... | 30-75 „ „ „ |
| $H_2SO_3$ ... | ... | 30-40 „ „ „ |
| Allyl sulphonic acid (salts of Na, K or Ni) | | 1-3 „ „ „ |
| Formaldehyde | ... | 0·3-0·8 „ „ „ |
| $\alpha$ and $\beta$ tri-chlor-butyraldehyde hydrate | | 0·2-0·5 „ „ „ |
| $p$H ... ... | ... | 3-5 „ „ „ |
| Temperature ... | ... | 40-50° C |
| Current Density | ... | 1-6 amps per sq. dm. |

However, the same firm, Udylite[39], is credited (1950) with a patent, the features of which summarize the claims of preceding patents. It will be useful, therefore, to discuss this patent at greater length with a view to clarifying better the long road travelled up to this point. The object of obtaining ductile and bright coatings is attained by using soluble organic compounds containing the aldehydic or ketonic carbonyl and/or the double olefinic bond.

While the $\alpha$ or $\beta$ unsaturated sulphonic acids like, for example, vinyl or allyl sulphonic acid, give bright coatings on polished surfaces, the rate of brightening of a matt surface is rather low or, rather, they do not rapidly improve the brightness of the original surface. If, however, one adds, for example, chloral hydrate, acetaldol or a mono- di- or tri- allyl amine in amounts varying between 0·05 and 0·15 gm. per litre, there is then soon produced a distinct and notable improvement, especially in the zone of relatively low current density.

The vinyl-allyl-sulphonic acids are excellent in respect of their capacity for maintaining the zones of low current density bright and adherent in spite of the presence of a perceptible amount of zinc as an impurity.

Excessively high concentrations cause brittleness in some cases. The baths can also even contain an amount as high as 75-100 gm. per litre of $CoCl_2 \cdot 6H_2O$ (or its equivalent as sulphate). Baths with nickel sulphamate or nickel fluoborate can also be employed.

The best $p$H values are between 3 and 5. Too low a $p$H (2·0-2·5) tends to slow down the rate of brightening. It is not possible to employ heating coils of lead, or lead-lined tanks, when using baths having a high chloride content (and low sulphate content) owing to lead being easily soluble in such baths.

Still in 1950, Freed and Stocker (per the Seymour Co.[40]) put in a claim for protection for a brightening agent formed from an aryl-aldehyde sulphonate and a reaction product from the action of sulphuric acid with an alykl-substituted mercapto-di-hydropyrimidine.

The Udylite Co. now created new baths with aldehydes, unsaturated ketones, with or without chromophoric groups and with aromatic sulpho-acids[41] and baths containing, besides the other constitutents, salts of thallium[42], while the E. I. Du Pont de Nemours Co. [43] introduced into their baths mainly 1·5 gm. per litre of methyl naphthalene sulphonate.

The 2-7 naphthalene-disulphonates of sodium or potassium in concentrations of the order of 3 to 4 gm. per litre have been studied in the nickel baths of Zdryavtsev, Korol'kova and Fedurkin[44]. These writers operated without agitating their baths at low current densities (0·1-2 amps per sq. dm.) and with agitation when working with a higher range of current densities (1·5 to 5 amps per $dm^2$). Brittle deposits were obtained only when the thicknesses obtained were greater than 25-30 microns.

Between 1948 and 1950 investigations were completed which had been based on the "reverse electro-clearing" principle (electrolytic polishing obtained by alternating the current from one pole to the other) of Nixon and Olsen[45], applying it to electrodeposition. Periodically reversing the current with the Jernstedt "PR" process, rapid and bright coatings were obtained—particularly of nickel[46].

Finally, quite recently, other Udylite patents have sought protection[47] for adding to the bath

of nickel of 0·001-0·002 grams per litre of C-substituted halides of N-alkyl-pyridine, quinoline or iso-quinoline, alternatively of 0·001 gm. per litre of C-substituted quinoline or iso-quinoline and 0·1-0·3 gm. per litre of alkyl or aryl sulphonamides or sulphonates of nickel, alternatively([48]) of 0·1-1·0 gm. per litre of carboxyalkyl halides of pyridine and 0·001-0·005 gm. litre of a compound of di-pyridyl: this jointly with 0·5 to 7 gm. per litre of a cyclic sulphonic acid or of a sulphonamide, alternatively([49]) of an aryl sulphinate (from 0·005 gm. per litre to saturation), like benzene or toluene sulphinate in baths of mixtures of the fluoborates of nickel and potassium. These patents protect, besides, the addition([50]) to a bath of conventional type of the following compounds: a pyrazole N-alkyl (from 1 to 6 atoms carbon) pyridine or quinoline (0·001 to 0·02 gm. per litre) and benzene sulphonamide, sulphonimide, benzene-sulphonic or naphthalene-sulphonic acid (from 0·02 gm. per litre to saturation).

One specific bath described consists of:—

| | |
|---|---|
| $NiSO_4 \cdot 6H_2O$ ... | 200-300 gm. per litre |
| $NiCl_2 \cdot 6H_2O$ ... | 125-145 ,, ,, ,, |
| $H_3BO_3$ ... ... | 40 ,, ,, ,, |
| *o*-benzoyl-sulphinimide | 1-2 ,, ,, ,, |
| *p*-toluene sulphonamide | 1 ,, ,, ,, |
| N-methyl-acetate 4 nitro-5 (-3° pyridine) pyrazol chloride ... | 0·002-0·006 gm. per litre |

This bath operates at 40-50° C with *p*H value 3-5.

The Harshaw patents include([51]): the addition of 0·05-0·5 gm. per litre of coumarin to fluoborate or sulphamate baths. The coumarin in these can be in the simple state or substituted by alkyl or acyl groups containing not more than 4 atoms of carbon. The *p*H is maintained between 2·5 and 5. Other people make use of brighteners consisting of aromatic compounds containing the C-$SO_2$ group as the most important constituent([52]) or of amino-polyalkyl substances([53]) with a molecular weight of over 100 and of a sulphonic acid derivative with an aromatic nucleus.

Bright and ductile electro-deposits are thus obtained from a fluoborate nickel bath and small amounts of sulphurated quinidine or benzoic sulphonimides([54]).

In this connexion it may be recalled that the fluoborate nickel bath (75 gm. per litre) at 54° C and using 10 amps per sq. dm. was introduced in 1950 by Roehl and Wesley([55]). This bath has the advantage of being able to work with a high current density, but obtains bright deposits by means of judicious additions of brighteners.

Young([56]) adopted, instead, the phosphate bath at temperatures between 25 and 85° C and used current densities between 2 and 12 amps per sq. dm. The electrolyte is prepared by dissolving nickel carbonate or trivalent nickel oxide ($Ni_2O_3$) at 105° C in phosphoric acid (density 1·379) with subsequent addition of alkaline phosphates which allow higher current densities to be used.

A bright and very ductile nickel coating is obtained from a bath developed by International Kenmore([57]), having a base mainly of hydrofluoric and boric acids and brighteners. The HF forms with the Ni a complex fluoride and guarantees a *p*H of between 1 and 6.

The bath contains at least 30 gm. per litre of metallic nickel. There are for preference present as brighteners, a mixture of *para*-toluene-sulphonamide, saccharine and fuchsine.

Also, unsaturated polyvalent (usually tertiary) alcohols, like dimethyl-acetylene-carbinol, have been successfully employed experimentally as agents for obtaining bright nickel when quantities between 0·1 and 1 gm. per litre are used([58]), and in the field of reducible dyestuffs zinc powder and hydrochloric acid have been tried in the presence of sodium bishulphite or hydrosulphite. In addition to fuchsine, which has already been mentioned, use has been made of *para*-rosaniline, methyl violet, aniline blue, aurine and similar substances ([59]).

Semi-bright deposits of nickel have been obtained by W. Canning and Co. Ltd.([60]) from a commercial bath containing 120-140 gm. per litre nickel sulphate, 15-60 gm. per litre nickel chloride, 5-30 gm. per litre formic acid, 30-40 gm. per litre boric acid and 1 gm. per litre coumarin. A *p*H between 2·1 and 2·5 was used. The bath could also contain 0·5 gm. per litre formaldehyde and up to 150 gm. per litre magnesium sulphate. It is operated for preference at 60-80° C and with a current density of 4-6 amps per sq. dm.

Among the baths most recently put into operation, may be mentioned that of United Chromium Inc.([61]), which makes use of a primary brightener of the indazole type (0·005 to 0·05 gm. per litre) and of a secondary (subsidiary) brightener of the aryl sulphonate type. Note should also be taken of the solution of Wagner Bros. Inc., who prefer to add 0·01-1 per cent. of *iso*-thiourea-propionic acid([62]).

Sodium carboxy-methyl cellulose is used as a brightening agent in electro-plating, either nickel or cadmium. One particular patented bath([63]) contains sodium cyanide and 0·05 to 0·1 per cent. of the brightener.

R. Blasberg([64]) introduces enzymes or ferments into a bright nickel-plating bath of the Watts type in order to improve its action.

A bath recently developed by Harshaw([65]), enables the addition to be made of thio-phenol-sulphonic acid (0·15 gm. per litre). in the form of its nickel or cobalt derivatives, in combination with ethylene cyanohydrin (0·3 gm. per litre) and aromatic nitriles or sulphonates. With this bath

*Continued in page 316*)

# *MEASUREMENT OF GLOSS in Vitreous Enamels*

## New Method Developed by U.S. Bureau of Standards

A SIGNIFICANT improvement in the stability and consistency of specular gloss measurements is made possible by a standardized method recently developed at the U.S. National Bureau of Standards. Intended primarily for application to porcelain enamels, the method has established sizes and tolerances for the critical geometric dimensions of specular glossmeters. The resulting gloss scale, following a recommendation of the Porcelain Enamel Institute of the United States, closely approximates that of the widely-used Hunter multipurpose reflectometer.

The task of determining the instrumental geometry required to duplicate the gloss scale of the Hunter reflectometer was undertaken by I. Nimeroff and H. K. Hammond, III, of the Bureau's photometry and colorimetry laboratory and J. C. Richmond and J. R. Crandall of the enamelled-metals laboratory. On the basis of their work, gloss tests for porcelain enamels have been included in the methods recommended by the P.E.I. and the American Society for Testing Materials.

Gloss measurement in the past has been used principally to evaluate the resistance of high-gloss enamels to abrasion or chemical attack. Usually specimens are measured, before and after attack, on the same instrument in the same laboratory. The data thus obtained are useful for determining relative resistance to attack even though a standardized gloss scale is not used. Serious difficulties arise, however, when an attempt is made to compare readings of non-standard glossmeters in different laboratories. A further impulse towards standardization has come in the last few years from the development of porcelain enamels in a wide range of gloss. These enamels make heavy demands on uniformity of product and matching of components made in different plants.

Specular gloss may be defined as the fraction of light flux reflected in the direction of mirror reflection (the specular direction) when the sample is illuminated by a parallel beam of light. In the case of enamels the angle of incidence (and reflection) is taken as 45 degrees. When measuring the gloss of paints, an incidence angle of 60 degrees is more common. If the fraction mentioned is multiplied by 1,000, the gloss is given in conventional "gloss units". For enamels the specular gloss is the fraction of light energy, in parts per thousand,

*Goniophotometer used by the U.S. National Bureau of Standards in standardization of glossmeters for measuring specular gloss of porcelain enamels and other ceramic materials. The purpose was to determine the sizes and tolerances of glossmeter source and receptor apertures which most nearly duplicate the gloss scale of the Hunter multipurpose reflectometer. Previous studies showed these dimensions to be crucial for the duplicability of glossmeter readings. Light from within aluminium box near operator's hand goes through a rectangular window, is collimated, strikes the specimen (held vertically in frame at centre of picture) and is reflected into the receptor arm at right. There the light is again collimated and goes through another rectangular window into the spherical integrating enclosure at extreme right of receptor arm. Angles of incidence and reflection, both of which could be varied, were fixed at 45° for this study. The operator is holding the removable brass plate containing the adjustable source window. The receptor window (not visible) is similarly adjustable in size. The e m f. of three series-connected photocells in the integrating enclosure is measured by the galvanometer and slidewire potentiometer at lower left.*

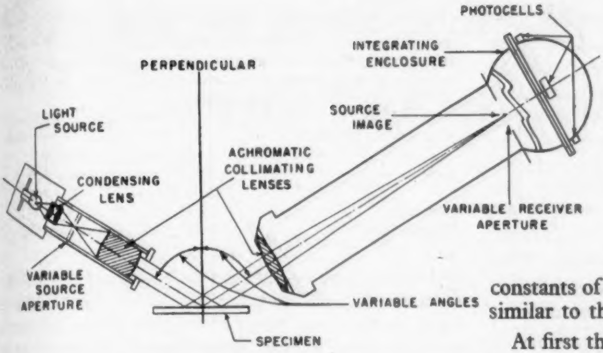



*Diagram showing essential components of the U.S. National Bureau of Standards' goniophotometer used in standardizing specular gloss measurements of porcelain enamels.*

reflected at 45 degrees when the specimen is illuminated at 45 degrees.

Unfortunately, strictly parallel beams are not obtainable, nor can the light reflected in the specular direction be perfectly separated from that in adjacent directions. The Bureau's present studies have shown that disregard of the effects of angular spread among the incident rays (aperture of the source) and among the reflected rays (aperture of the receptor) is largely responsible for the discrepant result obtained with different glossmeters.

In practical glossmeters a beam of light issues from a source, falls on the specimen, and is reflected through a rectangular window into a receptor where its intensity is measured either photoelectrically or in some other manner. The source is oriented with its long dimension perpendicular to the plane of measurement, that is, the plane determined by a ray from the centre of the source and the normal to the specimen at the point of incidence. Since the source is rectangular, the spread of light in the beam will vary in different planes through the optical axis. In this case it is customary to define the "aperture of the source" as the *pair* of angles that measure the spread in the planes perpendicular and parallel, respectively, to the plane of measurement. The long dimension of the receptor window is oriented like that of the source, and the "aperture of the receptor" is similarly defined as a pair of angles.

When the Bureau, acting on a proposal of the P.E.I. Quality Development Committee, took up the problem of glossmeter standardization, an instrument devised at the Bureau in 1936, the Hunter multipurpose reflectometer, was already in wide use and provided a convenient scale of values. Although sufficiently accurate for relative measurements on a single instrument, the glossmeter section of the Hunter reflectometer was designed before the importance of accurate control of field angle was appreciated. In general, therefore, its readings vary from one instrument to another. The problem then was to determine the geometric constants of a glossmeter that would provide a scale similar to that of the Hunter instrument.

At first the possibility was considered of making a direct measurement of the geometry of a Hunter instrument. However, the complexity of the Hunter optical system made such a determination unfeasible. Instead, a special goniophotometer was used as a glossmeter, and its source and receiver apertures were adjusted by trial to duplicate the desired scale and thus to establish the geometry requirements.

The goniophotometer used had been constructed for earlier studies. It is basically a device for throwing a beam of light on to a specimen at any desired angle of incidence and for measuring the light reflected in any direction in the plane of measurement. Light is provided by a standard headlight bulb. Its filament is brought to a focus in the plane of the source window, which thus becomes the effective source. Light from the window is collimated by an achromatic lens before falling on the specimen. The reflected light goes through another achromatic collimating lens which, if the specimen had a mirror surface, would form an image of the source in the receptor window. Then the light enters an integrating sphere in which three phototubes, connected in series, measure the total flux through the receptor window.

Since space conservation was not a problem, the instrument was made sufficiently large to permit measurement of its components with high geometric accuracy. It is so constructed that one can control accurately and independently (1) both dimensions of the rectangular source and receptor windows; (2) angles of illumination and view; (3) beam collimation; and (4) position of source image relative to the receptor window.

One of the Bureau's Hunter instruments was chosen for comparative study. With it the gloss of nearly one hundred specimens was measured. The instrument was set up in the usual manner with the gloss opening in a horizontal position and a sample of appropriate reflectance in position to furnish the comparison beam. The gloss scale was adjusted for linearity by inserting calibrated neutral filters in the gloss beam in front of the receiver window.

Two fundamental considerations guided the

trial-and-error process for determining the angular size of the goniophotometer source and receptor (apertures) that give readings in agreement with the Hunter multipurpose instrument. First, it was shown that glossmeter readings for highly diffusing (low-gloss) specimens are almost completely independent of the size of the source. Readings for such specimens are directly proportional to the angular size of the receptor entrance window, the cosine of the specular angle (in this case 45 degrees), and the diffuse reflectance of the specimen. Thus a multipurpose instrument gloss reading for a highly diffusing specimen of known reflectance permits calculation of the angular size of the receptor window of that instrument.

Second, readings for high-gloss specimens depend primarily on the size of the source relative to the receptor size. If the source is too large, reflected rays that should enter the receptor are blocked by the entrance window and a low reading results. If the source is too small, reflected rays that deviate too far from the specular angle are permitted to enter the receptor and a high reading results. Therefore, once the receptor aperture had been chosen, the trials for determining the source aperture could be restricted to high-gloss specimens.

To minimize the work, a criterion on scale duplication was set. This criterion required that for the 100 specimens selected the gloss reading obtained on the adjusted goniophotometer should not differ generally from that obtained on the multipurpose instrument by more than 5 gloss units.

The dimensions of the rectangular source and receptor apertures thus determined were 2·7 degrees × 1·8 degrees and 9·9 degrees × 7·9 degrees, respectively. With slight modification and addition of tolerances, this glossmeter geometry was ultimately recommended to the P.E.I. and A.S.T.M. for incorporation in their test methods. The receptor aperture was rounded off to whole degrees. With slight scale modification, the angular source size in the plane of measurement was reduced, and that perpendicular to this plane increased, to permit easier utilization of existing lamp filaments. Aperture tolerances were chosen partly on the basis of experience with similar tolerances for 60-degree specular gloss geometry and partly on the basis of the present investigation. The recommended glossmeter apertures and tolerances of the P.E.I. and A.S.T.M. proposed methods are given in the Table.

It should be noted that specular gloss is but one of several factors that are related to the quality of gloss as perceived by the eye. Porcelain enamels happen to fall in the range, 1 to 100 gloss units, for which specular gloss correlates well with the perceived quality. For surfaces of lower gloss, however, such as paper and flat paints, the eye seems to be guided more by reflection at grazing angles and by the contrast between reflection in the specular direction and that in other directions. On the other hand, in the gloss range above that of the enamels, distinctness of images and absence of bloom or haze about them become the decisive factors influencing the visual judgment. Moreover, there are still other factors that must be taken into account in special sitations.

In addition, in the specular gloss range, it is often possible to distinguish the specular component in the reflected light from that which is diffused more or less uniformly in all directions. It is now generally considered desirable to correct measurements of specular gloss by subtracting the contribution made by the diffuse component, although so far only rough approximations to the magnitude of the latter are possible in most cases.

TABLE I

*Recommended glossmeter apertures and tolerances, parallel and perpendicular to the plane of measurement, for 45°. specular gloss of ceramic materials, P.E.I. and A.S.T.M. test methods.*

| Measurement Plant | Aperture and Tolerance | |
|---|---|---|
| | Source | Receiver |
| | degrees | degrees |
| Parallel ... ... ... | $1.4 \pm 0.4$ | $8.0 \pm 0.1$ |
| Perpendicular ... ... | $3.0 \pm 1.0$ | $10.0 \pm 0.2$ |

**REFERENCES**

(1) Nimerhoff, I., Hammond H. K., Richmond, J. C., and Crandall J. R. "Specular Gloss Measurements of Ceramic Materials," *J. Am. Ceramic Soc.*, 1956, March, **39** (3).

(2) "Gloss Test for Porcelain Enamels," Bulletin T-18 of the Porcelain Enamel Institute; "Tentative Method of Test for 45-deg. Specular Gloss," A.S.T.M. designation C346-54T.

(3) Hammond, H. K., Nimeroff, I. "Measurement of Sixty-degree Specular Gloss," *J. Research N.B.S.*, 1950, **44**, p. 585 (RP2105).

(4) Hunter, Richard S. "Methods of Determining Gloss," *J. Research N.B.S.*, 1937, **18**, **19** (RP598); Harrison, V. G. W. "Definition and Measurement of Gloss," P.A.T.R.A., Cambridge, England 1945.

## Bright Nickel Plating

(*Continued from page 313*)

one can also operate with impurites, which in other baths would cause grey patches to appear.

In Japan, in 1953([66]), there was patented a brightening agent consisting mainly of cadmium, zinc and sulpho-cyanide for addition to nickel-plating baths.

It should be emphasized, however, that an excess of brightener usually has harmful effects on the physical properites of the deposits([67]). Copper and zinc in unregulated quantities are the usual—and extremely harmful—contaminating substances in nickel-plating baths. According to observations made by Patching([68]), these can be removed from plating solutions by being plated out at a *p*H of 2·5-3 with a current density of 0·05-0·1 amps per sq. dm. in the case of copper and 0·2-0·3 amps per sq. dm. in the case of zinc.

# A Review of Industrial Methods for THE CHEMICAL BRIGHTENING OF ALUMINIUM

By A. W. BRACE, A.I.M. *

*(A Paper presented at the 6th International Mechanical Engineering Congress, Paris, June, 1956)*

*Synopsis*

*During recent years industrial methods have been developed for the production of bright finishes on aluminium and its alloys using chemical processes. These have the merit of simplicity of operation and control. The two principal types of chemical brightening baths are those based on phosphoric acid and those containing nitric acid and ammonium bifluoride. In this paper the effects of varying the composition and operating conditions of these baths on the results obtained is discussed with reference also to the influence of metal purity. Anodizing technique and methods of testing bright anodized finishes are also considered.*

### Introduction

FOR many years most of the articles produced commercially with a bright finish have been obtained by nickel-chromium plating. The most significant event of recent years in the surface treatment of aluminium and its alloys has been the introduction of bright anodized finishes whose appearance compares favourably with that obtained from chromium plating. The term "bright anodized" has been used for convenience of terminology, but it also serves as a reminder that the final result is dependent upon the combination of the brightening and anodizing processes.

While electrobrightening techniques have been used successfully in industry for a number of years, they suffer from several important disadvantages if mass production of bright anodized articles is to be undertaken. In the case of the older processes, such as Brytal(1), the standard of pre-polishing must be high since the process of brightening produces little macro-smoothing. The more recently developed electro polishing solutions(2) can exert an appreciable smoothing action but require high current densities. In both cases, problems arise in jigging, the provision of auxiliary cathodes, etc., to ensure uniform treatment, and movement of the anodes is sometimes necessary to ensure absence of gas streaking.

Chemical brightening requiring no electrical current does not have these disadvantages, and apart from the installation of suitable equipment, the main control required is additions of an appropriate "make-up" solution or compound to the bath. The time of treatment is usually 1 to 3 min., which is more in keeping with mass-production requirements.

However, although chemical brightening treatments employed industrially will brighten most grades of aluminium, the appearance of the final bright anodized article will depend upon the quality and purity of the metal used. While there is undoubtedly a field of application of bright anodizing to lower purity commercial materials, the equivalent of the chromium plate finish can only be obtained by the use of anodizing quality "super-purity" (99·99 per cent.) aluminium or alloys based on it. This will be discussed in greater detail in a subsequent section.

### Principles of Chemical Brightening

There is at present some confusion of terminology in the literature and the terms "brightening" and "polishing" are used somewhat indiscriminately. In the author's opinion it is somewhat misleading to refer to these treatments as "chemical polishing" since they tend to suggest that their effect is similar to that of mechanical polishing, which is not so. All of these processes produce an increase in brightness of the surface, but many of them do not give any appreciable smoothing action.

The mechanism of chemical brightening has been discussed in accounts appearing in various journals(3) and these reveal that it is by no means fully understood. It seems essential to employ a substance which is capable of dissolving aluminium but there must also be present an oxidizing agent which will maintain a thin, probably porous, oxide film on the surface. Provided that the oxide film is sufficiently stable to ensure that random attack takes place (as opposed to local, preferential grain-boundary attack as in etching), then brightening will result. The most common oxidizing agent is nitric acid, while phosphoric acid or hydrofluoric acid (usually as ammonium bifluoride) are the usual attacking media.

* Aluminium Laboratories Limited, Banbury, England.

Since the processes do not depend upon external current they are usually operated at elevated temperatures—up to 110° C—since raising the temperature increases the current generated internally by the local corrosion cells formed. Some brightening mixtures tend to be somewhat viscous, and it is believed that a viscous layer is formed somewhat similar to that found in electropolishing. Some very dilute baths will brighten satisfactorily but in general their smoothing action is slight.

## Types of Industrial Chemical Brightening Mixtures

In this section it is proposed to discuss briefly the influence of composition on the operating characteristics of chemical brightening mixtures. These are of two principal types—(*a*) those based on phosphoric acid, and (*b*) those containing ammonium bifluoride (or hydrofluoric acid) and nitric acid. Others have appeared in patents, particularly containing alkalis, but as far as is known, these either give little brightening effect, or are too violent in reaction for industrial use.

### (*a*) *Phosphoric-acid Based Solutions*

The first chemical brightening mixture used in Great Britain consisted of 75 per cent. phosphoric acid, 25 per cent. sulphuric acid (by vol.)[4], but although bright the surface does not possess that characteristic image clarity which is normally associated with bright finishes. Subsequently other compositions were developed which produce a bright, highly specular finish, although still with a slightly greater diffuse component than is found on chromium plate.

An essential constituent of these baths, apart from phosphoric acid, is nitric acid, which is normally present to the extent of at least 3 per cent. (by vol.), while other acids such as sulphuric, acetic or boric may also be present. The following are the typical compositions of some commercial mixtures as far as can be ascertained:—

| *Kynalbrite* [5] | *Alcoa R.5* [6] | *Alupol IV* [7] |
|---|---|---|
| Phosphoric acid 78 per cent. | Phosphoric acid 73 per cent. | Phosphoric acid 40 per cent. |
| Sulphuric acid 11 per cent. | Nitric acid 4 per cent. | Sulphuric acid 25 per cent. |
| Nitric acid 11 per cent. | Acetic acid 10 per cent. | Boric acid 5 per cent. |
| +0.1 per cent. $FeSO_4.7H_2O$ | Water 13 per cent. | Nitric acid 30 per cent. |
| | +0.1 per cent. $Cu(NO_3)_2$ | |

These baths are normally operated at about 100° C with treatment times ranging from 1 to 5 min. In view of the wide differences in composition quoted in the patents, it is necessary to discuss the influence of each constituent on the operating characteristics of the bath.

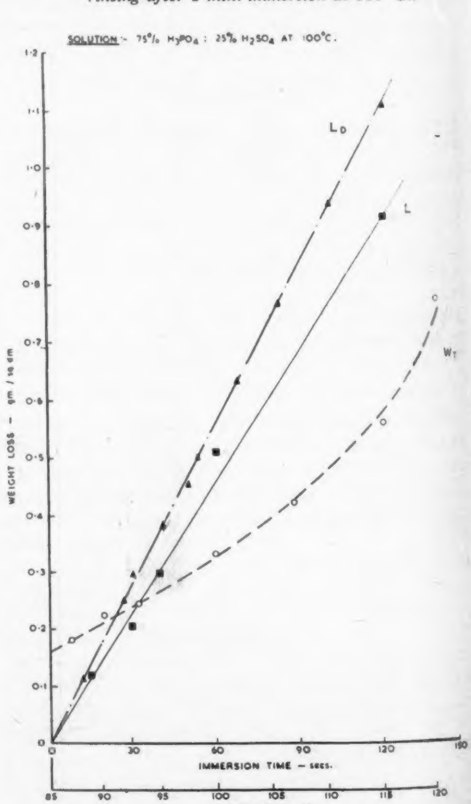
Experiments have been carried out by the author and a colleague[8] to obtain data on these factors. Tests were made on the response of commercial-purity aluminium to mixtures based on phosphoric acid. By first using a 75 per cent. phosphoric-acid, 25 per cent. sulphuric-acid (by vol.) mixture at 100° C, and then substituting 5 per cent. nitric acid for an equal volume of sulphuric acid, the beneficial effect of nitric acid on the specular reflectivity was confirmed. The influence of temperature and time of immersion on weight loss were also studied and these are reproduced graphically in Figs. 1 and 2. Similar studies were made using 75 per cent. phosphoric acid, 20 per cent. acetic acid, 5 per cent. nitric acid, and 75 per cent. phosphoric acid, 20 per cent. water, 5 per cent. nitric acid. The values for weight loss-time of immersion, and weight loss/temperature are given in Figs. 3 and 4.

*Fig.* 1—*Effects of immersion time, temperature and delay in rinsing on weight loss of aluminium* (*SIC*) *in* 75 *per cent. phosphoric-acid*/25 *per cent. sulphuric-acid brightening solution.*

$W_T$ = *Weight-loss/temperature relationship*, 1-*min. treatment.*

$L_I$ = *Weight-loss/time relationship for instant rinsing after* 1-*min. immersion at* 100° *C.*

$L_D$ = *Weight-loss/time relationship for* 45-*sec. delay in rinsing after* 1-*min. immersion at* 100° *C.*



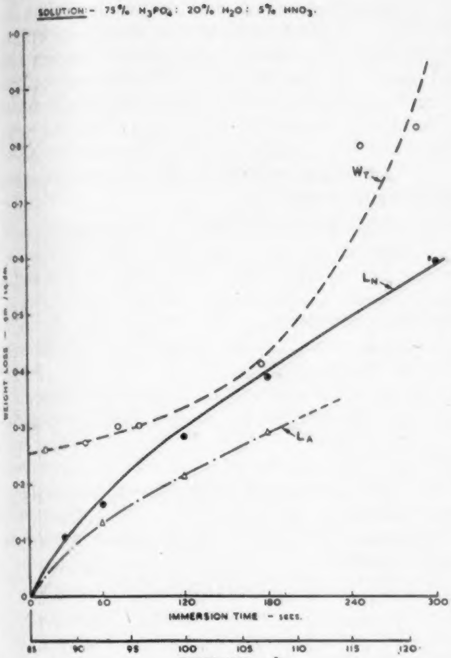



*Fig. 2.—Effect of immersion time, temperature and aluminium content on weight loss of aluminium (SIC) in 75 per cent. phosphoric-acid/20 per cent. sulphuric-acid/5 per cent. nitric-acid brightening solution.*

$W_T$ = *Weight-loss/temperature relationship for 3-min. immersion.*

$L_N$ = *Weight-loss/time relationship for immersion in new bath at 100° C.*

$L_A$ = *Weight-loss/time relationship for aged bath at 100° C containing 9·56 gm. per litre aluminium.*

These reveal some interesting trends of practical importance. It appears that sulphuric acid is mainly a cheap diluent for phosphoric acid. Comparison of Fig. 1 and Fig. 2 shows that nitric acid significantly affects the characteristics of the time/weight-loss curve, and the rapid change in slope in the first minute probably indicates a period of formation and stabilization of the oxide film. The rapid increase in the amount of metal removed with rise in temperature is also significant. High nitric-acid contents, however, appreciably increase the volume of fumes evolved.

The effect of acetic acid appears to be to reduce the rate of attack, particularly as the temperature rises, so there appears to be some benefit in its presence since it minimizes the possibility of undesirable effects due to rise in operating temperature which may occur on account of the exothermic nature of the brightening reaction. Water tends to slightly increase the rate of attack, but increases the maximum aluminium content which can be tolerated in the bath. With the phosphoric/sulphuric/nitric-acid mixture the maximum aluminium content at which satisfactory brightening could be obtained was around 12 gm. per litre, but this was increased to 20 gm. per litre with the phosphoric/water/nitric-acid mixture.

These results seem to indicate that a bath of the Alcoa R.5 type has the best all-round operating characteristics. A study made of the R.5 bath by the author's colleague, Dr. R. C. Spooner(9), showed that by careful control of composition, it was possible to obtain reasonable brightening with aluminium contents up to 37·5 gm. per litre, although Alcoa have never claimed a higher working limit than 25 gm. per litre.

In all brightening mixtures nitric acid is decomposed and requires replenishment from time to time. Most anodizers make regular additions and it is possible with experience to ascertain from the appearance of the brightened surface when the nitric acid is low but before actual etching takes place. Analytical methods have been devised for estimation of nitric acid based on reduction of nitric acid by ferrous-ammonium sulphate. Water may also volatilize more readily than the phosphoric acid and it can be estimated by the Karl Fischer technique. With the R.5 bath it was found that the additions required corresponded approximately to 45 per cent. nitric acid, 45 per cent. water, and 10 per cent. acetic acid (by vol.) added daily to make up drag-out losses and the basic solution

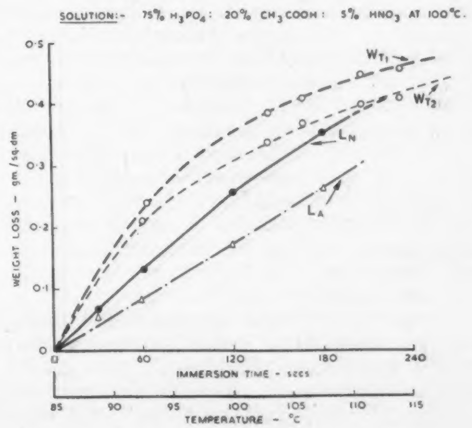
*Fig. 3.—Effect of immersion time and aluminium content on weight loss of aluminium (materials SIB and SIC) in 75 per cent. phosphoric-acid/20 per cent. sulphuric-acid/5 per cent. nitric-acid solution.*

$W_{T_1}$ = *Weight-loss/temperature relationship for SIC after 3-min. immersion.*

$W_{T_2}$ = *Weight-loss/temperature relationship for SIB after 3-min. immersion.*

$L_N$ = *Weight-loss/time relationship for new bath at 100° C.*

I = *Weight-loss/time relationship for bath at 100° C with 6·88 gm. per litre aluminium content.*



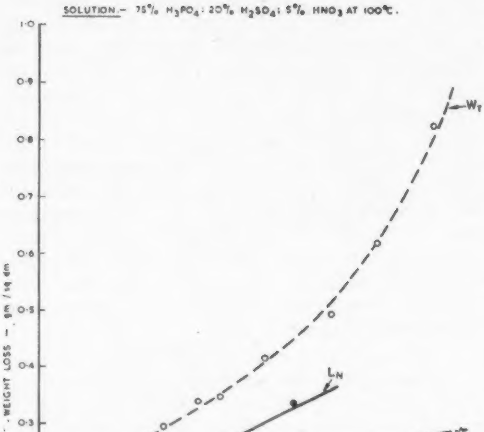



*Fig. 4.—Effect of immersion time, temperature and aluminium content on weight loss of aluminium (SIC) in 75 per cent. phosphoric-acid/20 per cent. water/5 per cent. nitric-acid solution.*
WT = *Weight-loss/temperature relationship for 3-min. immersion.*
LN = *Weight-loss/time relationship for new bath at 100° C.*
LA = *Weight-loss/time relationship for bath at 100° C with 5·92 gm. per litre aluminium.*

added once a week. These figures are given as a guide and may vary with operating conditions.

*(b) Nitric-acid/Ammonium-bifluoride Mixtures*

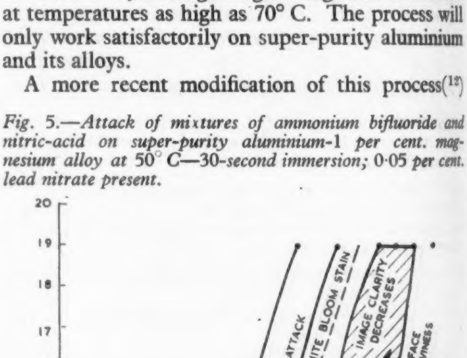
The best known process of the type operated commercially in Europe is the Erftwerk process, invented by Vereinigte Aluminium Werke[10], which is often quoted as of the nominal composition 16 per cent. ammonium bifluoride, 13 per cent. nitric acid (by weight), but this is in fact near the upper limit of its operating range. Studies made of this process at Aluminium Laboratories Ltd., Banbury[11] show the effects of composition on brightening characteristics to be those given in Fig. 5. It will be seen that in fact there is some advantage in lowering the bifluoride and nitric-acid contents by 1 to 2 per cent. The time of treatment required is only 15 to 30 sec.

The amount of metal removed is appreciable, and the process has a definite smoothing effect since it will remove the scratches produced by 160-grit abrasive mops, although the image clarity is reduced if this preparation is used. The effect of bifluoride content and immersion time on thickness of metal removed is shown in Fig. 6. In the usual operating range 0·001 in. to 0·002 in. of metal are dissolved in 15 to 30 sec. by this treatment. When the ammonium-bifluoride content is low the work tends to show a white frosted appearance but low nitric-acid concentrations tend to result in a bright but etched surface, often with some preferential attack.

The lead content of the bath is important since it is present as an impurity in the commercial bifluoride. While a small amount of it is essential for optimum results, beyond about 0·08 per cent. there is a deterioration. This means that the commercial material should preferably contain only 0·10 per cent. lead since there is a risk of lead build-up if more bifluoride is added to compensate for that consumed—the amount required is about 1 lb. for each 6 to 10 sq. ft. of work processed. The operating temperature should be maintained at 50 to 60° C, although brightening can be obtained at temperatures as high as 70° C. The process will only work satisfactorily on super-purity aluminium and its alloys.

A more recent modification of this process[12]

*Fig. 5.—Attack of mixtures of ammonium bifluoride and nitric-acid on super-purity aluminium-1 per cent. magnesium alloy at 50° C—30-second immersion; 0·05 per cent. lead nitrate present.*



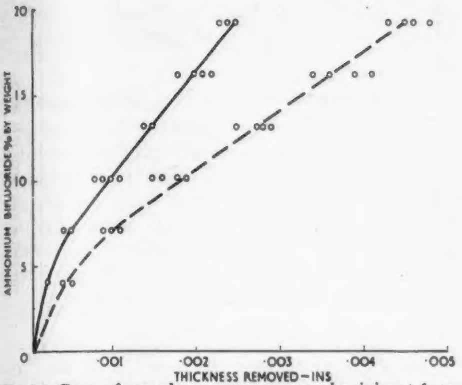



*Fig. 6.—Rate of attack on super-purity aluminium + 1 per cent. magnesium in nitric-acid/ammonium-bifluoride solutions at 50 to 60° C. Plotted points represent different contents of nitric acid.*

is based on the addition of about 1 per cent. dextrin to the basic Erftwerk bath. This has several useful advantages—the rate of attack is reduced by about 40 per cent. and it can be operated at a slightly lower temperature. The solution will brighten aluminium of lower purity *e.g.*, 99·7 per cent., and the specular reflectivity is higher and comparable with that obtained by Brytal electrobrightening. On the other hand, it has less smoothing action and a fairly good mechanical polish is necessary.

The preparation of the material for brightening is simple, and primarily involves degreasing in vapour or emulsion cleaners as required, followed by a light caustic etch, rinse and dip in nitric.

The flow sequence for Erftwerk brightening is the following:—

Degrease

↓

Etch ½ to 1 min. in 10 per cent. NaCH at 50° C

↓

Rinse

↓

1 min. in 50 per cent. nitric acid

↓

Erftwerk brighten 20 to 30 sec.

↓

Rinse

↓

Anodize

↓

Seal

Where the supply water is hard there is an advantage in quenching the work in 50 per cent. nitric acid after brightening to prevent scum formation. The work can also be held in a 1 per cent. sodium-dichromate or chromic-acid solution prior to anodizing. It should always be rinsed in water before and after anodizing.

In the United States brightening baths containing nitric acid and ammonium bifluoride have been used commercially, but these are more dilute. The following are the nominal compositions of two such mixtures as given in the patent literature:—

| | *Kaiser*[13] | *General Motors*[14] |
|---|---|---|
| Nitric acid | 2·5 per cent. | 5·0 per cent. |
| Ammonium bifluoride | 0·6 per cent. | 0·6 per cent. |
| Chromic acid | 0·6 per cent. | 0·6 per cent. |
| Glycerol | 0·6 per cent. | — |
| Ethylene glycol | — | 0·6 per cent. |

These baths are operated near boiling point (93 to 98° C) and treatment times of 3 to 5 minutes are customary. The brightener has virtually no macro-smoothing action so that where the maximum specularity is required on a plain surface, good mechanical polishing is necessary.

A disadvantage of this type of bath, is that it is relatively quickly exhausted and continuous replenishment is necessary. While this can soon be ascertained by experience, it still presents problems if the bath is to be used in an automatic plant. It will give satisfactory brightening on most grades of aluminium.

## Influence of Metal Composition and Structure

It has already been established by Pullen[15] that the total reflectivity obtained after electrobrightening and anodizing increases with the purity of the metal. The reflectivity obtained after chemical brightening in phosphoric-based mixtures prior to anodizing is higher than that obtained by electrobrightening on the lower purities. This is due to the tendency of such mixtures to dissolve out the intermetallic constituents on the surface, thus leaving it of higher purity than the core of the material.

This effect is clearly demonstrated in Fig. 7, taken from an account by Helling and Neunzig[16], which shows the influence of anodic coating thickness on the total and specular reflectivities obtained after brightening aluminium of various purities in a commercial phosphoric acid (Alupol IV) bath. While there is a slight fall in reflectivity for super-purity (99·99 per cent.) aluminium-magnesium alloys it is small in relation to that produced on 99·8 per cent. and 99·5 per cent. purity metal. The effect on the specular component is more marked than that of the total reflectivity. This means that an image viewed in the brightened surface appears "blurred" and gives the impression of not being bright even though the total reflectivity of brightened 99·5 per cent. aluminium is higher than that of chromium plate.

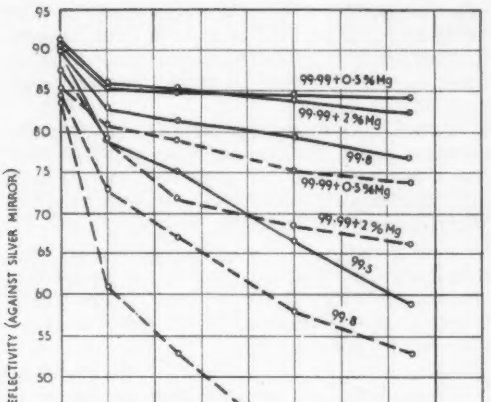



*Fig. 7.—Effect of metal purity and anodic film thickness on total and specular reflectivity (after W. Helling and H. Neunzig* (16)*.*

While metal of 99·5 per cent. purity brightened and anodized to a film thickness of 2 to 5$\mu$ has been widely used for cheap mass-produced jewellery and cosmetic cases, it is essential to use super-purity aluminium for arduous applications, such as motor-car trim where an appearance similar to that of chromium plate is required. On the other hand for architectural applications, or where the surface is broken by patterns, fluting, etc., quite an attractive result is obtained with lower purities (99·5 to 99·8 per cent. aluminium). The response to colour anodizing and the depth of colour is enhanced by brightening. Bright anodizing demands a high metallurgical standard if the material is to be used in forms with relative large unbroken surfaces, since the smallest imperfections are revealed. It is essential in these applications that anodizing quality material should be used. Mottling or the appearance of a "grainy" structure are defects of metallurgical origin, while streaks in the surface are associated with pick-up of dirt during rolling. If not severe these may be often removed by a light polish, although treatment with a 180-grit abrasive prior to buffing may also be necessary.

### Equipment for Chemical Brightening

The equipment for chemical brightening is relatively simple, but the highly corrosive chemicals employed present problems in the choice of suitable materials. Provision has to be made for adequate exhaustion of the fumes produced, particularly with phosphoric-acid mixtures containing nitric acid. Here again it is convenient to discuss these problems separately for the two main types of processes.

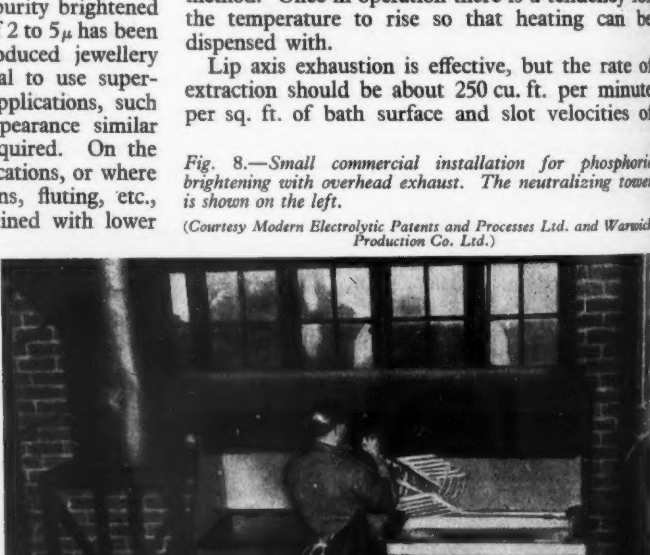
(A) *Phosphoric-acid Based Solutions*

The most universally used material for these baths is stainless steel of the stabilized 18/8 type or chemically pure lead, 12 lb. per sq. ft. weight, although the author has seen an installation in which a high-silicon acid-resisting cast iron was successfully used for some time. For preference the tank should be surrounded by an oil jacket containing immersion heaters in the bottom. Direct heating of the solution with stainless-steel-covered immersion heaters is possible, but the temperature distribution is less uniform. High-pressure steam coils immersed in the tank are an alternative heating method. Once in operation there is a tendency for the temperature to rise so that heating can be dispensed with.

Lip axis exhaustion is effective, but the rate of extraction should be about 250 cu. ft. per minute per sq. ft. of bath surface and slot velocities of

*Fig. 8.—Small commercial installation for phosphoric brightening with overhead exhaust. The neutralizing tower is shown on the left.*

*(Courtesy Modern Electrolytic Patents and Processes Ltd. and Warwick Production Co. Ltd.)*



2,000 to 3,000 ft. per min. The ducts can be of material coated with acid-resisting paint, but PVC is preferred. For large units a hood surrounding three sides of the tank is often used (Fig. 8) in addition to lip axis exhaustion since there are still residual fumes produced as the work is removed from the tank prior to rinsing.

Owing to their objectionable nature fumes should not be exhausted direct to the air, but should be washed first. Several supply houses have designed self-contained units for this purpose, but surprisingly efficient fume removal can be obtained by use of two concentric glazed soil pipes filled with coke with water flowing over it.

(B) *Nitric-acid/Ammonium-bifluoride Mixtures*

These compositions attack stainless steel very rapidly, and for the Erftwerk bath a satisfactory material is mild-steel lined with $\frac{1}{16}$-in. polythene. Although there is no long experience of this process in Great Britain it also appears that butyl rubber is a satisfactory lining. Exhaust ducting can be of PVC although wood or galvanized steel coated with acid-resisting paint provides a cheaper but much less durable alternative.

The tank can be heated by steam coils placed in the bottom, although on small units an outer jacket of water or oil, electrically heated, has some advantages. To obtain optimum results it may be necessary to provide cooling once the tank has reached temperature.

One of the attractions of this process is that despite its high nitric acid content there are no obnoxious brown fumes produced, as with phosphoric-nitric mixtures. While the same general conditions for rate of fume extraction should be observed as for phosphoric-acid brighteners, lip exhaustion should prove adequate. There is, in fact, some advantage in arranging to exhaust air from one side and blow air from the other since this produces some additional cooling of the surface of the solution which otherwise tends to overheat.

## Anodizing Technique

It is becoming more widely appreciated that the anodizing conditions determine the properties of the anodic film. Stronger electrolytes, high bath temperatures and low anodizing voltages give soft porous films; there is some evidence to show that their corrosion resistance is less than that produced in weak electrolytes. For many engineering applications a moderately hard and abrasion-resistant film is required particularly for automobile trim, refrigerators and other domestic appliance parts.

For such applications a 3N. sulphuric-acid electrolyte (15 per cent. by weight) is preferred, and the temperature should be controlled at 55 to 60° F and the current density 15 amp. per sq. ft. giving a rate of film formation of 25 to 30$\mu$ per hour. This involves provision of refrigeration equipment, but this is essential if good abrasion resistance is to be obtained. It has some compensations in that the area of work that can be processed in the bath can be increased over the amount determined by the working rule of 1 amp. per gallon of electrolyte.

Sealing of the anodic coating after brightening and anodizing is important since it affects the general corrosion resistance of the coating. It is desirable to seal in either deionized, distilled or very soft water since a film of scum due to insoluble calcium salts will form on the surface if hard water is used. In Germany steam sealing is used by some anodizers to overcome this difficulty, but steam sealing is slower than sealing in boiling water. The *p*H of the sealing water should either be checked daily or the water renewed daily, since there is a danger of residual sulphuric acid being carried over into the sealing tank and so producing a low *p*H which will make sealing ineffective; a *p*H of 5.5 to 6.0 is preferred.

## Testing of Bright Anodized Finishes

There is always a danger that bright anodized finishes will give unsatisfactory performance due to the use of very thin anodic coatings on low-purity material. Good methods of testing are essential to the purchaser who wishes to ensure their reliability and equally important to the anodizer who desires to maintain a good reputation. The main testing methods are summarized below in respect of measuring film thickness, brightness, abrasion resistance and corrosion resistance.

(A) *Film Thickness*

There is no absolutely reliable non-destructive test for film thickness, but some use has been made of the electrical breakdown voltage test for this purpose. This method is not popular in Great Britain because there are too many variables that can affect the result. Materials of commercial purity can give unreliable values due to imperfections in the anodic film formed over intermetallic constituents. The anodizing conditions also have some effect, and although reasonable results may be obtained under one set of conditions they are not always the same for other anodizing conditions. The method of carrying out the test is also by no means standardized.

Direct measurement under a microscope or stripping a small off-cut or test-piece still remain the reference methods for film thickness checks.

(B) *Brightness*

This tends to be a subjective quality and the results obtained by instruments do not always correspond with the visual assessment made by the eye. British Standard 1615 uses the Guild Reflectometer as the reference method; this measures the

total amount of light from a point source which falls on a photocell after being reflected from the bright anodized surface. This is expressed as a percentage of the light reflected by a silver mirror. A shutter which can be placed across the reflected beam enables the diffuse reflected light to be measured and this is expressed as a percentage of the total and gives a useful guide to the image clarity which the eye tends to assess when judging brightness.

A useful inspection tool, however, is the illuminated grid (Fig. 9) which consists of a ¼-in. black mesh printed transparent paper and affixed to a ground glass screen which covers a box about 10 in. × 10 in. The screen is illuminated from behind by a lamp of suitable power. If brightened samples are tilted at 45 degrees to the screen and gradually withdrawn from the illuminated grid a point will be revealed when the grid squares become blurred and indistinct. It is not difficult to fix a minimum distance representing an acceptance level.

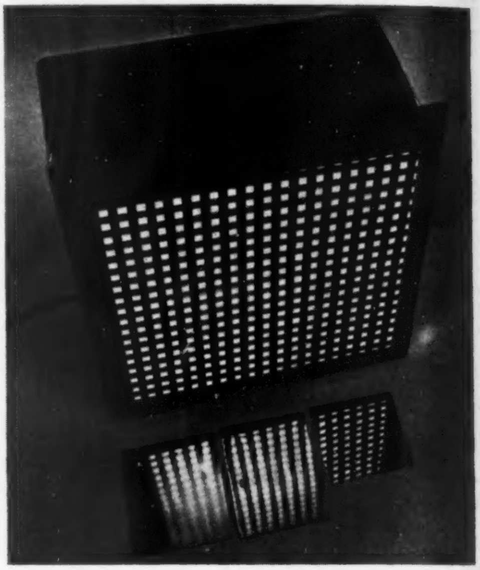


*Fig. 9.—Illuminated grid for comparison of image clarity of bright anodized aluminium.*

(C) *Abrasion Resistance*

While tests have been devised for rubbing of the anodic coating with an abrasive disc under a standard load, a simpler and often more rapid method is that based on the Schuh and Kern technique. With this test a stream of 150-mesh carborundum powder is directed at low air pressure (5 or 10 cm. of mercury) on to the surface of a flat anodized specimen held at 45 degrees to the nozzle. A small black spot appears when the coating has been penetrated. The abrasion resistance is determined by the number of grams of abrasive required to penetrate the coating, but for comparative purposes is best expressed in terms of grams per $\mu$ of coating.

(D) *Corrosion Resistance*

The corrosion resistance of anodic coatings is high, much better than that of nickel-chromium plating, and it is difficult to find a satisfactory accelerated test. The most potentially useful tests are those which primarily assess the efficiency of sealing. In Germany the Kesternich test ([17]) has been used, and this subjects bright anodized articles to a humid atmosphere in a cabinet of 300 litres containing 2 litres of water in which 2 litres of sulphur dioxide and 2 litres of carbon dioxide have been dissolved. The water is maintained at 50 to 55° C, and the articles are subject to five cycles of 8 hours in the cabinet and 16 hours in the atmosphere. Inadequate sealing is revealed by the formation of a whitish bloom on the surface. From preliminary work there is some evidence that other conditions than the above are satisfactory provided a humid $SO_2$ atmosphere is maintained.

Some use has been made of an accelerated test in which the anodized component is immersed for six days at room temperature in a solution of 2·5 per cent. sodium chloride, 1·5 per cent. acetic acid, 0·1 per cent. hydrogen peroxide (by weight). The amount of pitting developed by the end of the test period is influenced by both metal purity and anodic film thickness. Inadequate data is available to assess the correlation between this and service performance and the test should be used with caution. However, there is adequate experience to show that with 10 to 15 $\mu$ film thickness the performance of correctly processed bright anodized aluminium is superior to that of nickel-chromium plate to BS 1224-Ni 12 which is the principal bright finish at present used commercially.

## References


(1) British Patent 449,162.
(2) British Patents 526,854, 612,478, 645,453, 675,186.
(3) Fischer, A. and Koch, L. *Metall*, 1952, **6**, (17/18), pp. 491-496. Koch, L. and Kest, S. *Metall*, 1953, **7**, (15/16), pp. 577-581. Brace, A. W. *Metal Finishing Journal*, 1955, **1**, (6), pp. 253-258, 278; (7), pp. 312-323, 332.
(4) British Patent 625,834.
(5) *Light Metals*, 1954, **17**, (200), pp. 348-349.
(6) British Patent 659,747.
(7) British Patent 675,444.
(8) Brace, A. W. and de Gromoboy, T. S. *Trans. Inst. Met. Finishing*, 1956, **33**. Advance Copy No. 2.
(9) Spooner, R. C. Aluminium Laboratories Limited, Kingston, Internal Report.
(10) British Patents 693,776 and 693,876.
(11) Gardam, G. E. and Peek, R. *Trans. Inst. Metal Finishing*, 1956, **33**, Advance Copy No. 3.
(12) British Patent 738,711.
(13) U.S. Patents 2,593,447, 2,593,448, 2,620,265.
(14) U.S. Patent 2,614,913.
(15) Pullen, N.D. *J. Inst. Metals*, 1936, **59**, pp. 151-158.
(16) Helling, W. and Neunzig, H. *Aluminium*, 1952, **28**, (9), pp. 289-295.
(17) Kesternich, W. *Stahl. u. Eisen*, 1951, **11**, pp. 587-588.

# CHROMIUM DIFFUSION

## and its Application to Sheet-Metal Parts

By R. L. SAMUEL, Ing., Chim., A.I.M.* and N. A. LOCKINGTON, M.A., A.R.I.C., A.I.M.*

*(A Paper presented to the Conference on "Modern Processes" organized by the Sheet and Strip Metal Users' Technical Association at the Charing Cross Hotel, London, on April 26 and 27, 1956)*

### Introduction

THE importance of surface treatments has noticeably increased during the last few years. There was a time when the word "coating" implied a cheap substitute for an existing material of proven properties, but the exacting requirements of modern engineering have caused a fundamental reappraisal of these views.

The designer has gradually acknowledged the fact that, while some properties such as tensile, impact strength, etc., are inherently dependent upon the mass of the article, many others, corrosion, thermal oxidation, wear resistance, etc., are primarily surface effects where the bulk of the article plays only a "supporting" role.

It is not the object, in this paper, to review surface treatments as a whole, but merely to define the position of diffusion processes, within this vast range that is now available to industry.

The first group, comprising non-metallic coatings, is primarily concerned with the protection of the metal surface against "static" conditions of use. In other words, it is implied that the surface will not be subjected to severe mechanical stress, or thermal changes. Such coatings broadly include: paints, varnishes, oxide films, resins, enamels, etc.

The second group covers metallic coatings which have been applied by methods such as chemical deposition, electroplating, "hot-dip" techniques, etc. Their object is to confer to the surface a temporary protection against surface corrosion and erosion, commensurate with the estimated "life" of the article. For the sake of clarity, this group may be called "cladding methods" as the deposited metal or alloy is, as a rule, a distinct adjunct to the metallic surface and adhers essentially by means of its cohesive strength. To this group may be added the newly developed vapour plating techniques where the metal is deposited at low pressure from the gas phase.

The third group, in which the authors are chiefly interested, covers all "diffusion techniques", and more particularly, chromium diffusion.

In contrast with "cladding" methods, the object here is not to cover the surface with a deposited metal, but rather to transform the outer strata of the article by alloying into it the requisite amount of another element which will alter the surface properties. The protecting element is not "put on", but "brought in".

Finally, in this introductory section, it is necessary to stress the difference between surface treatments and finishing treatments. Most of the techniques classified under groups I and II are "finishing processes", *i.e.*, they are applied at the final stage of manufacture when the article has been machined or fabricated and, as a consequence, one of their important functions is to improve the appearance and decorative standard of the surface apart from any other consideration.

On the other hand, many diffusion processes are not primarily designed as finishing techniques but are often best applied at an intermediate stage of manufacture.

### DIFFUSION PROCESSES

All usual diffusion processes differ from other types of surface protection, in so far as they imply some form of heat-treatment. The best-known instances of diffusion processes are carburizing and nitriding which are now universally accepted. Metallic diffusion processes are, comparatively, more recent additions.

Fundamentally, there is some analogy between carburizing and chromium diffusion; both imply the penetration of carbon or chromium into the metal surface, under the influence of heat. But, while carbon penetrates to a considerable depth at comparatively low concentration, chromium diffuses more superficially but forms a much richer alloy.

The reason for this is to be found in the different mechanisms of diffusion which apply to the small carbon atom (interstitial), and larger chromium atom (substitutional) within the steel lattice ([1,2,3]).

### Chromium Diffusion

Among the most recent industrial diffusion processes, chromium diffusion is of particular interest.

Chromium is one of the most useful alloying elements for iron, nickel, cobalt, etc. It confers improved properties for resistance to corrosion, thermal oxidation and wear or abrasion. Alloys of

*R. L. Samuel is Technical Director and N. A. Lockington is Chief Metallurgist at Diffusion Alloys L d., London Bridge House, London, S.E.1.

*Fig. 1 (left (×100).—Section through chromium-diffused mild steel, etched to show structure and coating*

*Fig. 2 (right).—Photomicrograph of section showing elongation of coating grains when a chromium-diffused mild-steel strip is bent*

iron and chromium, containing at least 13 per cent. of the latter, possesses all these properties.

It is now possible to obtain commercially on iron, nickel, cobalt or their alloys, surface coatings containing from 15 to 70 per cent. chromium, by applying diffusion methods.

*Conditions of Treatment*

Chromium is normally diffused into steel or other alloys by reaction of one of its halogen compounds at temperatures ranging from 800 to 1,100° C ([4,5]).

Several methods have been proposed, but a description will be given of the DAL process which is now commercially exploited on an increasing scale in this country, the U.S.A., Canada, France, etc.

The process is designed to ulitize conventional furnace equipment, and its essential features are:—

(1) A generating compound containing chromium and a solid "exchange" or "carrier" agent (ammonium iodide)([6]). This compound is prepared in powder form and is packed around the articles to be processed.

(2) Boxes similar to those used for pack-carburizing but fitted with a special "liquid" seal which prevents entry of gas during heating, processing and cooling([7]).

A typical processing cycle of 12 hours will give on low-carbon steel a coating of approximately 0·002 in. which averages 25 per cent. chromium in composition.

*Chromium-diffused Coatings*

The chromium-diffused coating is an alloy of chromium with the material of the article. A treatment carried out on mild steel will, therefore, give a coating of different composition from that obtained on a nickel- or cobalt-alloy workpiece.

(A) *Low-carbon Steels and Ferrous Alloys*

The alloy has a ferritic, columnar structure, and the average composition for a commercial treatment is of the order of 25 per cent. chromium.

The coating, generally of the order of 0·001 to 0·003 in., is ductile, and its hardness is of the order of 200 V.P.N. for low-carbon steel, to 400 V.P.N. for low-alloy, low-carbon steels.

(B) *High-carbon Steels and Cast Iron*

The surface alloy contains a high proportion of chromium carbide; its average chromium content is of the order of 50 to 60 per cent.

The coating, of the order of 0·0001 to 0·008 in. (according to conditions of treatment), is only moderately ductile, but of extreme hardness. Surface hardness may exceed 1,800 V.P.N.

(C) *High-alloy Ferritic and Austenitic Steels*

The coating shows always a ferritic structure of high chromium content, usually 50 per cent. or more. It is ductile, but of considerable hardness, usually above 600 V.P.N. and shows excellent frictional properties.

(D) *Nickel, Cobalt and Their Alloys*

The coatings vary considerably in composition according to the nature of the alloy, but the chromium content usually exceeds 30 per cent. It is normally ductile, but considerably harder than the original material.

## Chromium-diffused Thin-gauge Materials

The treatment of sheet or strip metal parts by chromium diffusion is particularly interesting as it is nearly always applied at an intermediate stage of the fabrication of the article.

As the process is carried out in furnaces, the

*Fig. 3.—Erichsen test on chromium-diffused mild steel*

utilization of box space is a vital factor in the economics of the treatment. Fabricated articles in sheet metal are often of complex shape so that the volume occupied is large in relation to the weight. Such articles would be costly to process and it is, therefore, generally the aim to process flat sections or blanks(8). In turn, this implies that the treated sheets or blanks must be capable of being formed, welded, etc.

### General Physical Properties of Chromium-diffused Sheet-metal Parts

Chromium-diffused mild-steel sheets have a light grey colour. The finish is matt but smooth and comparable to a lightly etched surface.

The coating itself is ductile and, provided that the underlying material is capable of withstanding mechanical deformation, the flat articles can be cold- or hot-rolled after treatment to a very considerable extent.

The following tests on chromium-diffused 16-s.w.g. low-carbon steel material give an idea of the permissible amount of bending:—

*Radius of Bend:*—1·5 mm.

*Furnace-cooled condition:*—Angle 60°—Coating undamaged. Angle 180°.—Minute stretch cracks at apex of coating.

*Normalized condition:*—Angle 180°.—Visible extension of coating—no failure.

The same material gives the following results on the Erichsen Test:—

| | Untreated | Chromium-diffused | |
|---|---|---|---|
| | | Furnace-cooled | Normalized |
| Start of "orange peel" effect on coating ... | — | 9·40 mm. | 10·5 mm. |
| Rupture ... ... | 12 mm. | 13·10 mm. | 12 mm. |

From this it can be seen that, in the correct condition, chromium-diffused sheet material can lend itself to comparatively severe forming operations.

The tensile properties of the treated material are naturally dependent upon the bulk of the section, and the coating, as such, plays no significant part, at any rate for sheet material of normal gauge. The effect may be more substantial for very thin sections, for example, gauges over 30 s.w.g. In connexion with tensile poperties, it must be remembered that furnace-cooled chromium-diffused material is in the annealed condition, and a normalizing treatment may be required in order to recover the original properties, if this is desirable.

Another important requirement of sheet metal is its weldability. Chromium-diffused steel is easily weldable. The weld may be effected by all normal techniques. When a rod is used, either for gas or electric welding, it is usual to utilize an austenitic 18/8 stainless rod (or, in some cases, a 25/20 H.R.

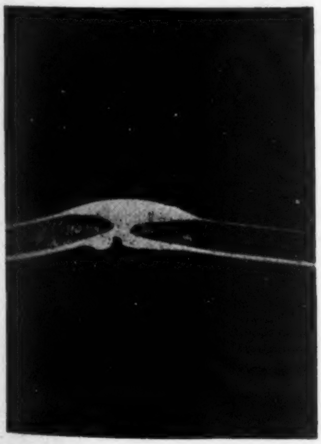
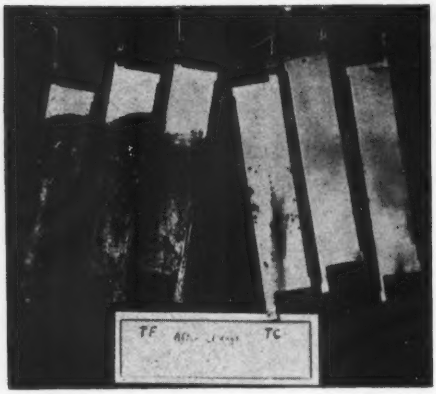


*Fig. 4 (left).—Section of chromium-diffused mild-steel tube, showing how the core, exposed by shearing, is protected by the austenitic weld metal.*

*Fig. 5 (right).—Chromium-diffused strips welded using 18/8 stainless rod. The mild-steel core has been dissolved in nitric acid leaving a "shell" of coating and weld metal.*




*Painted mild-steel specimens after 21 days in salt water. The three specimens on the right of each set were chromium-diffused before painting*

*Fig.* 6 (*left*). — *Undercoat and hard gloss finishing coat*

*Fig.* 7 (*right*). —*Finishing coat only*


steel rod) in order not to destroy the corrosion or heat-resisting properties of the fabricated article.

If the chromium-diffused sheet has been blanked after treatment and has, therefore, exposed edges, it is recommended to allow the weld metal to fill the gap as far as possible in order to eliminate any possible weakness along the weld line.

Tubes have been fabricated from blanked sheets having exposed edges, and both practical tests and micro-examinations have shown that the weld deposit had formed a continuous layer completely alloyed with the coating material without any mild steel remaining exposed.

In many cases, chromium-diffusion is carried out on already blanked parts, and this precaution is not necessary.

It might be mentioned that welding methods effected in the presence of an inert gas, such as "Argonarc", practically eliminate the discoloration on both sides of the weld line which is due to thermal oxidation.

TABLE I—*Tap Water Corrosion Test*

(*Samples immersed to half their height in glass beakers*)

| Sample | 1 Day | 1 Week | 1 Month | Ranking | Remarks |
|---|---|---|---|---|---|
| C.P.I. ... | — | — | — | V.G. | No corrosion whatever |
| C.P.II ... | — | — | — | V.G. | No corrosion whatever |
| C.W.S.I ... | — | L.(B.W.) | L.(B.W.) | F. | Light rust deposit developing at bottom of weld junction* |
| C.W.S.II ... | L.(B.W.) | L.(B.W.) | M.(B.W.) | P. | Medium rust deposit developing at bottom of weld junction* |
| C.W.D.I ... | — | — | L.(B.W.) | F. | Light rust deposit developing at bottom of weld junction* |
| C.W.D.II ... | — | 1.P.P.L. | 1.P.P.M. (B.W.) | P. | Medium rust deposit developing at bottom of weld junction. One pinpoint |
| 18/8.P.I ... | — | 1.P.P. | 1.P.P. | G. | One pinpoint of rust after one week. |
| 18/8.P.II ... | — | — | — | V.G. | No corrosion whatever |
| 18/8.W.S.I ... | L.W.C. | M.G.C. | H.G.C. | B. | Heavy general corrosion developing |
| 18/8.W.S.II ... | L.G.C. | H.G.C. | V.H.G.C. | B. | Very heavy general corrosion |
| 18/8.W.D.I ... | — | L.W.C. | L.W.C. | F. | Light weld corrosion* |
| 18/8.W.D.II ... | — | M.W.C. | M.W.C. | P. | Medium weld corrosion* |
| 13 Cr.P. I ... | — | — | — | V.G. | No corrosion whatever |
| 13 Cr.P.II ... | — | 1.P.P. | 1.P.P. | G. | One pinpoint of rust after one week |
| 13 Cr.W.S.I ... | L.W.C. | H.G.C. | V.H.G.C. | B. | Very heavy general corrosion |
| 13 Cr.W.S.II | L.W.C. | H.G.C. | V.H.G.C. | B. | Very heavy general corrosion |
| 13 Cr.W.D.I | — | — | L.W.C. | F. | Light weld corrosion* |
| 13 Cr.W.D.II... | — | L.W.C. | L.W.C. | F. | Light weld corrosion* |

* No general corrosion

P. Plain.
W.M. Welded scaled.
W.D. Welded descaled.

L.(B.W.) Light corrosion at bottom end of weld.
M.(B.W.) Medium " " "
L.W.C. Light weld corrosion.
M.W.C. Medium "
L.G.C. Light general corrosion.
H.G.C. Heavy " "
I.P.P. One pinpoint of rust.

V.G. Very good.
G. Good.
F. Fair.
P. Passable.
B. Bad.

Samples 2 in. × 1 in. × 18 s.w.g. Bright mild-steel sheet. Gas welding using 18/8 rod.

TABLE II—3 *per cent. Sodium Chloride. Half Immersion.* 15 *Days*

| Sample | 1 Day | 1 Week | 15 Days | Ranking | Remarks |
|---|---|---|---|---|---|
| C.P.I ... ... | — | — | — | V.G. | No corrosion whatever |
| C.P.II ... | — | 1.P.P. | 2.P.P. | F. | No general corrosion, but two pinpoints developing |
| C.W.S. ... | L.(B.W.) | M.(B.W. | M.(B.W.) I.P.P. | P. | Medium corrosion at bottom of weld junction |
| C.W.D. ... | L.(B.W.) | L.(B.W.) | L.(B.W.) | F. | Light corrosion at bottom of weld junction |
| 18/8.P.I ... | — | — | — | V.G. | No corrosion whatever |
| 18/8.P.II ... | — | — | — | V.G. | No corrosion whatever |
| 18/8.W.S. ... | M.G.C. | H.G.C. | V.H.G.C. | B. | Very heavy general corrosion |
| 18/8.W.D. ... | M.W.C. | M.W.C. | M.W.C. | P. | Medium corrosion along line of weld |
| 13 Cr.P.I ... | — | 1.P.P. | 1.P.P. | G. | No general corrosion—One localized pinpoint |
| 13 Cr.P.II ... | — | 1.P.P. | 1.P.P. | G. | No general corrosion—One localized pinpoint |
| 13 Cr.W.S. ... | M.G.C. | H.G.C. | V.H.G.C. | B. | Very heavy general corrosion |
| 13 Cr.W.D. ... | L.W.C. | M.W.C. 1.P.P. | M.W.C. 1.P.P. | P. | Medium corrosion along line of weld—one localized pinpoint |

Spot welding presents no special difficulty, but it should be noted that the setting adopted for untreated material may require adjustment if the best results are to be obtained on the chromium-diffused sheets. Under correct welding conditions, the weld junction partly diffuses into the core metal forming a chromium-rich alloy of considerable strength. In consequence, the spot weld is considerably stronger than the remainder of the sheet material.

Although copper brazing can be applied with some precautions in selection of temperature and flux, silver soldering gives much superior results, and its application offers no special difficulty.

Tin soldering is not possible with normal fluxing agents; the only satisfactory soldering operations have been obtained with phosphoric-acid flux.

### Resistance to Wet Corrosion

The chromium-diffused coating on mild steel is a high-chromium ferritic alloy and normally compares with the best quality chromium-iron alloys commercially available([9]).

Tables I, II and III give comparative results between chromium-diffused mild steel, 13 per cent. chromium-iron and 18/8 austenitic stainless steel, in both plain and welded conditions; in tap water, 3 per cent. sodium-chloride and 2 per cent. lactic-acid solutions.

TABLE III—2 *per cent. Lactic Acid Tests. Total Immersion.* 21 *Days*

| Sample | Grams, weight before | Grams, weight after | Grams, loss | Remarks |
|---|---|---|---|---|
| C.P.I ... ... ... | 12·035 | 12·035 | — | ——— |
| C.P.II ... ... | 12·123 | 12·122 | 0·001 | ——— |
| C.W.S.I ... ... | 12·926 | 12·870 | 0·056 | Solution slightly coloured* |
| C.W.S.II ... ... | 12·696 | 12·627 | 0·069 | Solution slightly coloured* |
| C.W.D.I ... ... | 12·8845 | 12·821 | 0·0635 | Solution very slightly coloured* |
| C.W.D.II ... ... | 12·8625 | 12·820 | 0·0425 | Solution very slightly coloured* |
| | | | | * Residue ferrous salt |
| 18/8.P.I ... ... | 11·187 | 11·186 | 0·001 | Solution very slightly coloured* |
| 18/8.P.II ... ... | 11·239 | 11·238 | 0·001 | Solution very slightly coloured* |
| 18/8.W.S.I ... ... | 12·092 | 11·979 | 0·113 | Strong yellow colouration* |
| 18/8.W.D.II ... ... | 11·795 | 11·7955 | 0·0005 | ——— |
| | | | | * Residue contains nickel and chromium |
| 13 Cr.P.I ... ... | 10·948 | 10·948 | — | ——— |
| 13 Cr.P.II ... ... | 10·926 | 10·926 | — | ——— |
| 13 Cr.W.S.I ... ... | 11·307 | 11·273 | 0·034 | Yellow solution—some residue* |
| 13 Cr.W.S.II ... | 11·3895 | 11·3575 | 0·032 | Yellow solution—some residue* |
| 13 Cr.W.D.II... ... | 11·3355 | 11·335 | 0·0005 | ——— |
| 13 Cr.W.D.II... ... | 11·535 | 11·531 | 0·004 | ——— |
| | | | | * Residue contains chromium |

The tables show that chromium-diffused mild steel has a resistance of the same order as chromium-iron and authenitic stainless steels in the "plain condition". In the welded condition, the chromium-diffused specimens usually were superior.

The most usual type of corrosion experienced with chromium-diffused sheets is "pin-point" corrosion. This is usually due to imperfections on the steel surface prior to treatment. The tendency to pin-point corrosion can normally be detected within 24 hours, by immersion in 3 per cent. sodium-chloride solution. It should be noted that little development takes place after the initial formation of the pin-point and that no real damage is caused as a result.

The following practical test illustrates the behaviour of the coating under severe weather conditions:—

Three types of mild-steel sheet loud-speakers were prepared:—

(*a*) Phosphated by proprietary process and stove-enamelled;

(*b*) Chromium-diffused, one-half left as processed, the other stove-enamelled on top of chromium coating;

(*c*) Stove-enamelled without prior surface treatment.

After two-months' exposure to winter weather conditions the following results were observed:—

*Type* (*a*)—Two areas of rust at junction of spring steel washers probably due to scratches of enamel paint on fitting;

*Type* (*b*)—No corrosion on either side;

*Type* (*c*)—Heavy general corrosion.

Some tests were also carried out on thinly chromized coatings to determine the adherence of paint and the behaviour of the painted samples to salt-water corrosion.

The preliminary tests showed that, after several weeks in salt water, the painted chromium-diffused specimens were practically intact, while the untreated painted samples were heavily corroded and paint had flaked off at several points. Long-term tests are being initiated in order to arrive at a more precise assessment of the improvement obtained by chromium-diffusion prior to painting or stove-enamelling.

Examples of sheet-metal applications for corrsion resistance include: sterilizing sinks, water and fuel tanks, trays, etc., for photographic processing, cooking utensils, such as frying pans and pie dishes, food processing equipment, etc.([10]).

To summarize, chromium-diffused sheet material is suitable for use in water (atmospheric corrosion), saline solutions (sea water), and weak organic acids (foodstuffs, milk, vegetable and fruit juices, etc.). The susceptibility to weld-junction corrosion is much reduced.

## Resistance to Thermal Oxidation

One of the most outstanding properties of chromium-diffused coatings is their high degree of resistance to scaling or thermal oxidation.

High-chromium alloys are known to possess such resistance, and the chromized coating having an average of 25 per cent. chromium (and around 50 per cent. near the surface) can be expected to withstand prolonged exposure at elevated temperatures.

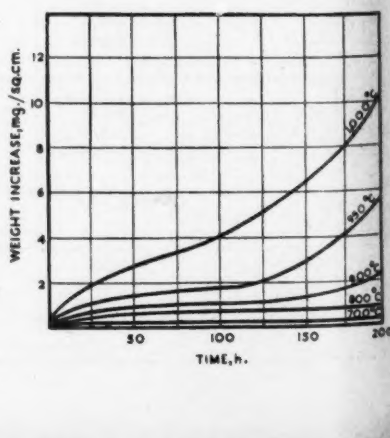
Perhaps the simplest way to assess the performance of chromium-diffused coatings is to consider the weight changes due to oxidation at various temperatures, in function of time.

Weight changes at temperatures of 700° C, 800° C, 900° C, 950° C and 1,000° C for chromium-diffused mild-steel sheet specimens are shown in Fig. 9.

For comparison purposes, the performance of various types of coated materials is given on a separate graph (Fig. 10) which collates results obtained for a 1,000 hours test by the Fulmer Research Institute([11]). It will be noticed that chromium-diffused steel has by far the lowest rate of oxidation.

*Fig.* 8 (*left*).—30-*in. gas-heated chromized sterilizing sink*
[*Courtesy of Liquid Measurements Ltd.*

*Fig.* 9 (*right*).—*Rate of oxidation of chromium - diffused mild steel* (0·15 *per cent. C*) *when heated in air at various temperatures*



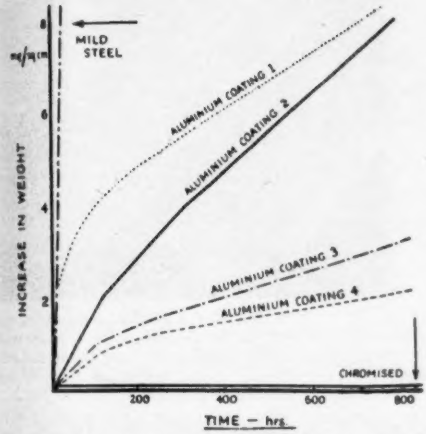



*Fig.* 10.—*Comparative resistance to oxidation at* 700° *C. of mild steel, and mild steel protected by chromizing and by various "aluminizing" treatments*
(*Adapted from Sully* et al, *ref.* 3)

The following figures illustrate this oxidation rate:—

TABLE IV

| Temperature of exposure in air | Weight increase in 200 hr. (mg. per sq. cm.) |
|---|---|
| Below 700° C | Not measurable |
| 700° C | 0·05 |
| 800° C | 0·70 |
| 900° C | 2·00 |
| 950° C | 5·00 |
| 1,000° C | 11·00 |

Under similar conditions, the rate of oxidation of untreated mild steel at 700° C is of the order of 70 mg. per sq. cm.

In terms of practical use, this means that, for temperatures up to 900° C the treated material can be used for very long periods without serious deterioration. Within the range of 950 to 1,000° C the effective protection will last for 300 to 500 hours.

These properties are used for many industrial applications of which the following are a few examples:—

Grill frets for gas cookers; radiant panels for infra-red drying ovens; perforated plates and sheet blanks for paraffin and oil space heaters; gas space heaters; flue pipes and sheet metal parts for all types of heating appliances; silencers and exhaust pipes and manifolds for I.C. engines; heat exchanger parts([12], [13]). In most instances, the flat blanks are treated and these are subsequently formed and welded. This method, which introduces the process at an intermediate stage of manufacture, has been shown in practice to be the most economical.

The use of chromium-diffusion for heat-resistance is by no means limited to mild steel. Many alloy materials are processed commercially, *viz.*, low-alloy steel sheets and blanks for heat-exchangers and boiler parts when a higher tensile strength is required. In addition, austenitic stainless or heat-resisting steels can be treated with advantage for the following reasons:—

(1) The rate of scaling is reduced. (A treated 18/8 steel has a lower rate of oxidation than an untreated 25/20).

(2) The sensitivity to sulphur-dioxide corrosion is practically eliminated and longer life is obtained in presence of products of combustion from gas or liquid fuels.

(3) The embrittlement due to intergranular corrosion is prevented, and parts can be reshaped even after prolonged heating.

(4) Weld junction areas are less sensitive to oxidation.

These properties are of value in the treatment

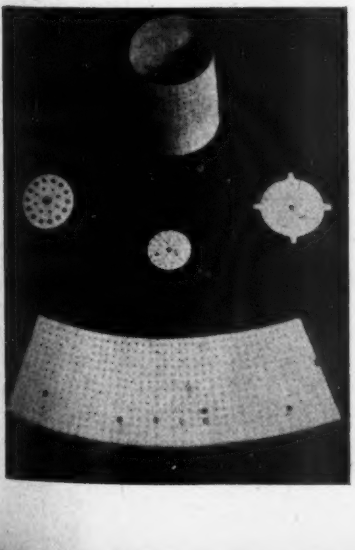


*Fig.* 11 (*left*).—*Chromium - diffused paraffin space-heater parts. Formed at top, blanks at lower end.*

*Fig.* 12 (*right*).—*Chromium - diffused grill fret assembly for domestic cooker*

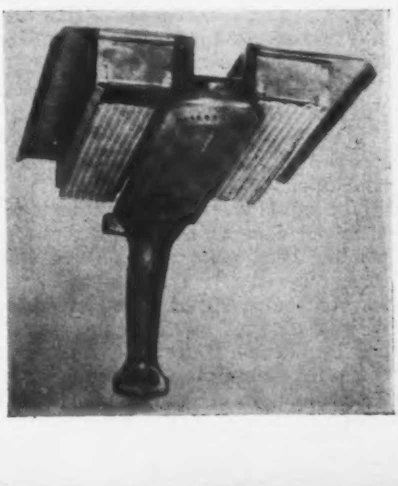
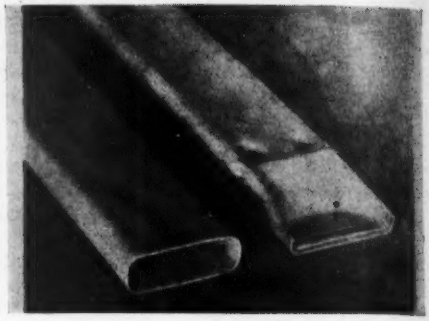


*Fig. 13.—Chromium-diffused shield and weld pins (right) go into the paint remover (left). The pins are projection welded into place*



[*Courtesy of the General Electric Co. Ltd.*

*Fig. 14.—Electric strip heater sheaths. These parts, made from formed and welded low-carbon steel are chromized after welding, then crimped to retain insulating material and heating elements*

of jigs and trays for heat-treatment, carburizing boxes, combustion chambers, turbine parts, etc.

Nickel and nickel-base alloys, in sheet form, are currently chromium-diffused. Although nickel-chromium alloys have, as a rule, a high degree of resistance to oxidation, this can be markedly improved by providing them with a surface richer in chromium. Research is now in progress on the properties of chromium-diffused nickel-and cobalt-base alloys which are widely used in the aircraft turbine field.

## Some Specialized Applications

The chromium-rich coating possesses some special properties which make it suitable for specialized uses. Three examples are given hereunder:—

(1) Tin solder does not "wet" the chromium-diffused surface, and copper brazing compounds do not normally adhere without special fluxing. The material can, therefore, safely be used for soldering and brazing jigs and fixtures, and is particularly useful for continuous plants.

(2) Chromium-diffused steels or nickel alloys give excellent glass-to-metal seals, and this property may find several applications in the electrical and electronics industries.

(3) The chromium-rich surface provides a very good undercoat for vitreous enamelling.

It is possible to provide a good-quality enamelling standard with a single coat of enamel without prior application of primer or undercoat.

The impact properties with a single coat of 0·005 in. of titanium-oxide frit show that a very strong bonding takes place during firing at the oxide-enamel interface. The thinness of the coating allows a limited amount of deformation or bending without cracking. The thermal shock properties are considerably superior to those of normal enamelled specimens. Flame impringement and quenching tests indicate a very high degree of resistance to "spalling" which may be due to a combination of efficient bonding coupled with the comparative thinness of the vitrified coating.

## Conclusions

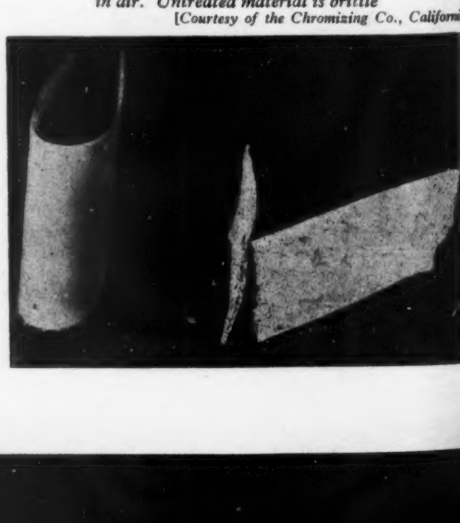
Chromium-diffusion is now commercially applied to a variety of sheet-metal parts for resistance to corrosion or heat.

In many of these applications the process is carried out on semi-finished parts where the maximum advantage is taken of the possibility of forming and welding. For this reason, it is important that the potential user should consider its application at the design stage and not only as a treatment to be given to the finished article.

The process is mainly applied to mild steel in order to make it corrosion- and heat-resistant and, in this respect, it may be considered chiefly on the grounds of economy. But, in the case of alloy steels or nickel alloys, the primary consideration is one of improved performance. In both cases chromium diffusion can bring a useful contribution to modern technology.

*Fig. 15.—Heat-resistance test. Chromium-diffused type 30 stainless steel remains ductile after 300 hours at 980° C in air. Untreated material is brittle*

[*Courtesy of the Chromizing Co., California*



## References


(1) Barrer, R. M. *Diffusion In and Through Solids*. 1941. Cam. Univ. Press.
(2) Laurent, P. *Metaux et Corrosion*. 1950, **25**, p. 172.
(3) Samuel, R. L. and Lockington, N.A. *Metal Treatment and Drop Forging*. 1951. **18**, p. 407, 415.
(4) Hoar, T. P. and Croom, E. A. G. *J. Iron and Steel Inst*. 1951, pp. 101-107.
(5) Sully, A. H. *Chromium*. 1954. Butterworths Scient. Publ.
(6) Samuel, R. L. British Patents No. 646,637 and 646,641.
(7) Samuel, R. L. British Patent No. 646,638.
(8) Samuel, R. L., Lockington, N. A. and Dorner, H. *Metal Treatment and Drop Forging*. 1955, **22** (117, 118, 119).
(9) Edwards, J. N. and Pearson, A. A. *Sheet Metal Industrite*. 1956. **33**, (345), p. 17.
(10) Samuel, R. L. and Lockington, N. A. *Iron and Coal Trades Review*. 1954, **169**, p. 803.
(11) Sully, A. H., Brandes, E. A. and Brown, R. H. *Metallurgia*. 1954. **49**, p. 165.
(12) Hollingum, J. *Machinist*. 1955, March 4, pp. 361, 367.
(13) Hollingum, J. *Metalworking Production*. **99**, 21, p. 925, 928.


## DISCUSSION

Mr. R. W. de Vere Stacpoole (Gillette Industries Ltd.) asked whether when chromizing small parts such as those used in a razor it was possible, having given the part a good surface finish beforehand, to retain that surface after the chromizing process. If so, would it be possible to process at the rate of about 50,000 small parts per day? The authors of the first paper had mentioned the possibility of putting chromizing on a continuous basis instead of on a batch production basis.

The authors had referred to testing for corrosion resistance and paint adhesion, and it was stated that with 3 per cent. sodium-chloride solution paint flaking was observed. He wondered, however, whether this was really a test of paint adhesion, which was normally thought of as resistance to mechanical damage. The authors stated later in the paper that excellent bonding was obtained with vitreous enamels, but was that bonding so much a property of the chromium as perhaps due to the nature of the surface which had been produced? He thought that it might be compared to a grit-blasted surface, and that the bonding was not due to the chromium at all.

On the question of corrosion, the authors referred to resistance to weak organic acids, but it would be of interest if they would say something about the resistance to vegetable and fruit juices and sulphur-bearing foodstuffs,

Mr. A. R. Muir (British Welding Research Association), said he had noticed that in the slide shown dealing with the metallography of the coatings, there were two distinct layers, and he wondered whether the inside layer, the one nearer the basis metal, was in fact the diffusion metal and the outer layer was a temperature deposition of chromium analogous to some extent at high temperatures to Mr. Aitken's nickel plating. He believed that the view had been put forward by Dr. Hoar two or three years ato that there was in some cases a growth in size of the part which became most important when it was a question of threaded components or something of that kind.

Second, in the case of low-carbon base material, at high temperatures, was it not a fact that the carbon tended to go to the coating, and if reliance was placed on carbon in the base material for strength, a considerable amount of strength was lost from the base material? Also, if the strength was obtained after heat treatment or cold working, again there must be a loss of strength. He also thought that the impact value of the material was lowered by the treatment, unless high-temperature normalizing was carried out afterwards. He suggested that the damage done could be repaired by heat treatment subsequent to chromizing, but it would be necessary either to use an inert atmosphere or to spoil the surface.

He had dealt with the chlorine process, using chlorine as a carrier, and there were one or two obvious differences which appeared to exist in using iodine rather than chlorine as a carrier. In the chlorine process, when chromizing high-carbon material, if the carbon was above about 0·35 per cent. they found that there was a network of fine cracking in the chromium coating, and on examination it was found that the columnar dendritic structure had been outlined on the grain boundaries by carbides, which was extremely damaging, to say the least, to the anti-corrosion properties.

Again, using the chlorine method they found that if they went above a specific temperature they had a great deal of trouble due to the adhesion of carbon to the surface of the coating, which was unsightly. Had the authors had the same difficulty in their process?

There had been a development in Germany six years ago called deep chrome, which allowed a sufficient depth of chromium to be put on for mechanical polishing to be done afterwards, so that a surface could be produced which was as good as, if not better than, chromium plating and which had a much better lustre than chromium plating.

### Use of Nimonic Alloys

He was interested to find that the authors were using the Nimonic alloys. Mr. Muir had once been concerned with the problem of discovering whether Nimonic had better scaling resistance when chromized. The answer had been given, however, before he had tackled the problem, and unfortunately it was wrong. He found that chromizing had no influence whatever in the direction of improving the scaling resistance, but in fact made it worse. The authors said that scaling resistance up to 900° C was satisfactory for a long time, but was it not a function of time and temperature? In other words, going up to 1,000 hours might be satisfactory at 800 or 850° C, but beyond 1,000 hours was there any guarantee that the chromium diffusion which would occur at that temperature, though slowly, would not affect the scaling resistance rather dis-

astrously at some specific time? There was the German idea that aluminium plus chromium, chromizing plus spraying with aluminium on the surface, would appear to be resistant up to 1,000 hours at 1,100° C. Mr. Muir thought that the comparison with aluminium coatings was not quite fair, since the aluminium coating would suck in oxygen and give a great increase of weight to start with, but would level off rather more rapidly than chromium plating.

Mr. R. L. Samuel, replying to the discussion, said that Mr. de Vere Stacpoole had put to him an important question about the treatment of small parts in very large quantities. There was nothing specially difficult about treating small parts, and he had processed very large quantities of parts which were only a little bigger than needles. Motor-car plug electrodes had been treated in very large quantities, and there had been no special difficulties. One of the reasons was that although the technique was a contact one the active agent was a gas, and therefore there was not the necessity for the very careful placing necessary in the case of a solid contact method. In some cases the adoption of high-frequency techniques of heating improved the efficiency of the process, particularly where large quantities of small parts were required.

The second question concerned the surface finish. With the present commercial method used for chromizing, the finish was not bright. It was possible to obtain bright finishes direct from the chromizing operation, but it required fairly high temperatures, which were not always recommended for the material; so that, although it could be done in theory, there was no really satisfactory method of obtaining directly a bright chromized surface at reasonable temperatures. It could be done, however, if there was a high enough temperature tolerance.

### Chromizing for Painting and Vitreous Enamelling

Another question related to the adhesion of paint. He was sorry that he had used that word, because it did not convey his meaning properly. The point was that various attempts had been made during the last few years to see the effect of light and very thin chromium-diffused coatings as an undercoat for various finishes, one of which was paint. At the same time the question had been raised of vitreous enamelling and of what was the real effect of chromium diffusion on the adhesion of a vitreous-enamel coat. It had been suggested that it might be a purely physical effect, presumably one of etching of the surface and nothing else. He himself doubted this. He did not think that so much trouble would have been taken to have undercoats for vitreous enamel if it had been a question only of physical contact, because it would be possible to shot-blast and use various other physical methods of treating the surface and improving the results, but not, he thought, to the extent which was wanted. More and more use was being made of thin nickel plating, so that it was generally admitted that, apart from the physical nature of the surface, there was something in the actual reaction at the interface between the enamel and metal which was beneficial.

He thought that the determining factor was the adherence of the oxide, first of all of the oxide of the metal to the metal itself, and then between the oxide and the vitreous enamel. The strength of the bond of the enamelled article depended on those two factors together, and it was well-known that chromium oxide, particularly if the oxidation was done under controlled conditions, was very firmly bonded to the underlying metal. That might explain the effect to some extent.

Another point on the subject of vitreous enamelling was that it was possible by the very fact of getting a good bond to reduce the thickness of the coating, and this was an advantage because as a rule the thinner the coating the better the thermal shock properties would be, and to some extent even the general properties of impact and flexing.

Vegetable and fruit juices came within the category of mild organic acids as a general rule. In some cases, particularly if one had citric acid and a lot of sugar, glucose and so on, the corrosive conditions would not be so mild, but on the whole the behaviour of the chromized coating should be similar to that of those usually considered suitable for such applications.

Mr. Muir, who was an authority on chromizing, had asked a number of questions. The first was on a metallographic point and concerned the photomicrograph which showed two distinct layers. It was probably true that the top layer was deposited chromium. It was very difficult to discriminate between the deposited and diffused chromium, because they were very much the same thing, and it was probable that the differentiations in etching which were apparent were due to the fact that on cooling a certain amount of chromium continues to be deposited.

Mr. Muir had then dealt with the effect of carbon and suggested that it created a barrier to the diffusion with the formation of carbides, which usually spoilt the corrosion-resisting properties of the material. That was not only due to the fact that chromium was diffused; it could be accelerated by the atmosphere in which the process was carried out. The conditions which Mr. Muir had in mind were highly reducing, which meant that there was a tendency for the diffusion of carbon from the inside to the surface, which made things much worse than they would otherwise be.

The second point concerned heat treatment, which Mr. Muir said was necessary in many cases of

(Continued in page 344

# Some Observations on THE INCIDENCE OF FISHSCALES on Enamelled Steel Pots

by Ing. E. MESSMER*

*A Paper presented to the 2nd International Enamelling Congress, Leamington Spa, 1955*

### Introduction

THIS paper, based on practical experience, may help to answer some general questions which are of particular interest to all vitreous enamellers.

Fishscales particularly appear in the production of heavy enamelled steel pots and pans and may have great influence on the economic operation of the plant.

The observations made later on presuppose the description of the programme of production as well as the different operations.

Two kinds of pots and pans are produced:

Lighter pots and pans for gas stoves, hereafter called " G "-pots.

Heavy pots and pans for electric stoves with concave bottoms, called " E "-pots for short.

### Process of Production

The quality of the steel sheets is of utmost importance, no less than the method and extent of deformation to which the material is subject during production of the pots.

*Quality of steel sheets*

Fine and medium steel sheets are used which are to-day standardized according to German Industrial Standard " DIN " 1623 under the group with good drawing and enamelling properties. Normally sheets of steel group V-23 are worked up. These sheets have a once-pickled surface and they must be free of scale; small scars and a slightly rough surface are permitted.

*Kind and degree of deformability*

The problem is to sell pots with good cooking characteristics, *i.e.*, good conductivity of heat from the stove to the pot, and equal distribution of the heat to the content of the pot. For these reasons the material at the bottom should be of heavy gauge, the sides being much thinner. The material at the bottom has always the thickness of the sheet and the sides are worked down to about 1.5 mm. by drawing and rolling on a specially constructed hydraulic rolling mill.

### Enamelling Process

All the frits for the enamelling are smelted in a rotary smelter and then quenched in water.

All raw pots and pans are annealed in an oxidizing atmosphere at about 900° C., and are then pickled in hydrochloric acid (18 per cent) at room temperature.

Both dipping and spraying are used, as appropriate, for the application of the enamel.

*Enamelling*

All pots, pans and covers, up to a diameter of 280 mm. get an inside and outside ground coat and

* Württemburgische Metallwarenfabrik

*Fig. 1—"G" and "E" pots, pans and covers.*

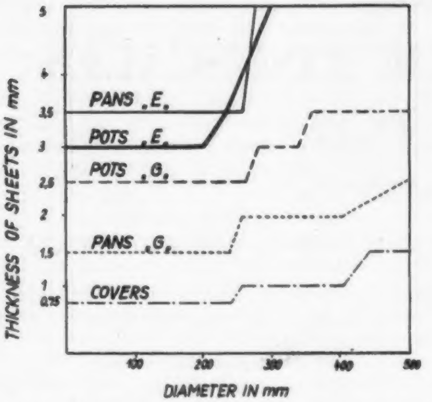



*Fig. 2—Thickness of material for pots, pans and covers.*

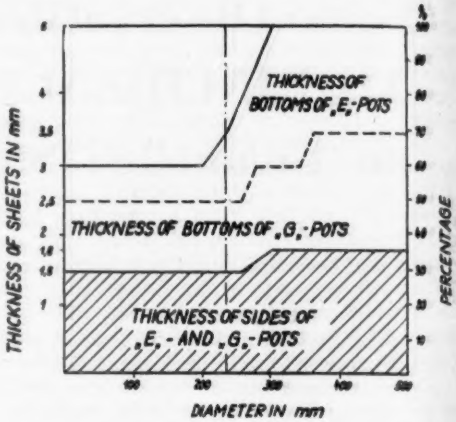



*Fig. 4—Difference of thickness between bottom and sides of pots for gas and electric stoves.*

one final cover coat. Larger dimensions differ in their outside coat. For them a special cover coat has been developed so that the big differences of the material could be overcome. The main characteristics of this coat are: high firing range, good conductivity of heat, a certain permeability to gas.

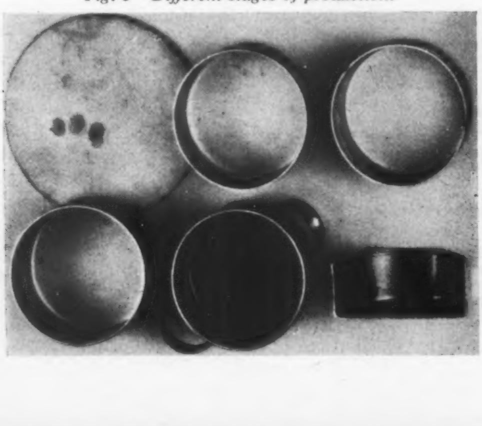
*Firing conditions*

All pots, pans and covers are fired in an automatic, electric controlled and heated furnace with a rotating core. The ware is charged and discharged by an automatic charging machine. The core of the furnace rotates, has 18 forks, and no heating system. The heating systems are placed in the side, bottom and ceiling. The firing temperature is about 920° C.

**Observations of Appearance of Fishscales in Practice**

During the last 3 years any appearance of fishscales has been statistically registered and so a really good basis exists for a critical observation.

*Fig. 3—Different stages of production.*



Consideration of all the different articles leads to the following results:

*Covers*

No fishscales could be found on covers in the period of observation. Covers showed some fishscaling too in the years shortly after the war, when only frits, low in adhering oxides, and borate content were available.

*" G " Pans and Pots*

The percentage of fishscales found on pans is well below 1 per cent.

There have been short periods of higher amounts of fishscaling on pots, but the average quantity lies in a range of 0.5 to 1.0 per cent during the whole period of observation.

*" E " pans or pots*

Fishscales on pans appeared in only a few cases in the last 2 years, the percentage being under 1.0 per cent.

On pots up to a diameter of 240 mm. fishscales appear at an increasing rate. Fig. 6 shows the quantity of fishscales on " E "-pots in the years 1953, 1954 and 1955.

To get comparable figures the month with the highest percentage of fishscales (March, 1953) was taken as a basis of 100 per cent.

The result of these observations was that fishscales crop up almost exclusively on the outside of the pots. The preferred location is the zone in the centre of the outer sides of the pot, *i.e.*, from a distance of about 20 mm. from the bottom, up to about 20 mm. from the rim of the pots.

Furthermore it is striking that the quantity of fishscales on the attacked pots increases with the height of the pots. Fig. 7 shows the percentage of

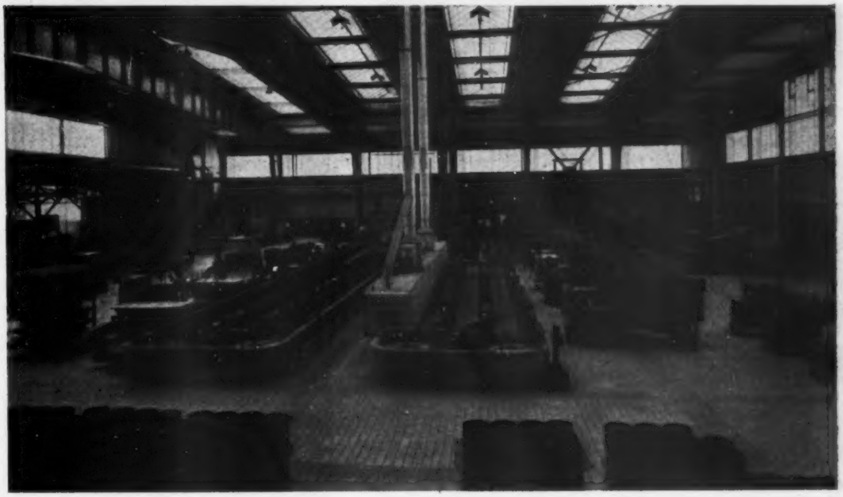


Fig. 5—General view of enamelling plant.

fishscales occurring on the four types of pots in production.

The kinds of fishscales which occur are shown in Figs. 8a to d and can be divided into four groups:

(*a*) Fishscales in ground coat; they appear after the drying of the cover coat or shortly after entering the oven for the final firing. Fishscales of this kind appear only rarely.

(*b*) Fishscales, which have a longest dimension in one direction of about 5 mm., which penetrate as far as the ground coat and sometimes even reach the surface of the steel sheet; these fishscales again were only very rarely encountered.

(*c*) Fishscales with a lengthwise dimension of about 3 mm. and a depth which penetrates the covercoat only, were the commonest. Normally only single fishscales were spread over the pots here and there, but sometimes small and occasionally large conglomerations of them were found.

(*d*) The last kind of fishscales, known in the literature as shiners, appear only seldom. Shiners are fishscales of a very small size—longest dimension about 0.5 mm.—and they appear mainly if the pot gets one cover coat alone without ground coat.

" E "-pans and pots are controlled on fishscales after a storage period of 15 days or in case of

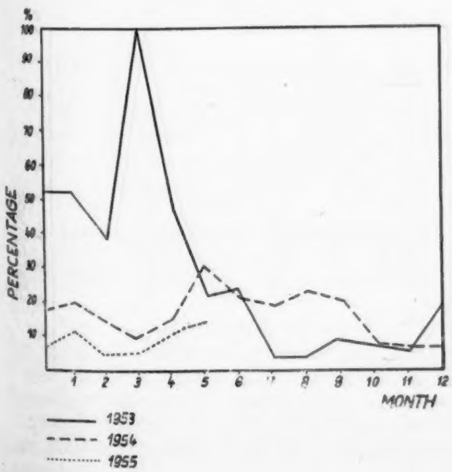



*Fig. 6 (left)—Graphs showing fishscales on "E" pots up to 240mm. dia.*

*Fig. 7 (right)—Proportion, in per cent, of fishscales on "E" pots up to 240 mm. dia. The amount of fishscaling is given for the different types of pots.*

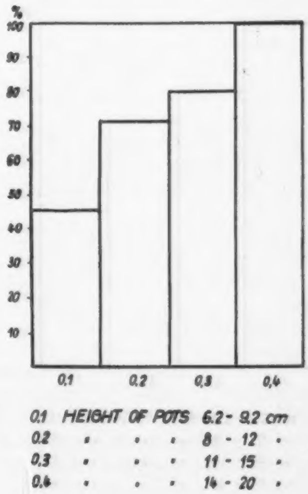


*Fig. 8a—Fishscales in ground coat.*

*Fig. 8b—Rare type of fishscaling. These penetrate the ground coat and sometimes reach to the surface of the steel sheet.*

special urgency after a heating period of 3 hours at 200° C.

In general fishscaled work is de-enamelled by sandblasting or in caustic soda solution.

The following comparison of the percentage occurrence of fishscales on newly enamelled as against de-enamelled and then re-enamelled "E"-pots is interesting.

(*a*) lower pots, height 6 to 9 cm.:
- newly enamelled ... ... 45 per cent
- de-enamelled and re-enamelled ... ... ... ... 45 per cent

(*b*) higher pots, height 14 to 20 cm.:
- newly enamelled ... ... 100 per cent
- de-enamelled and re-enamelled ... ... ... .. 69 per cent

These percentages are not based on reality, but on the equivalents of Fig. 7.

In both cases a remarkable decrease of fishscales could be observed especially on the "E"-pots with higher shape.

## Discussion of Findings

*Covers*

Fishscales on covers were found only—as already mentioned—when frits poor in borates and adhering oxides were used. The formation of gas can be quoted as one of the main causes of the complex conditions leading to fishscales or favouring their appearance.

H. Hoff and J. Klärding(1) have described the chemical reaction during fusing between the released steam and the steel sheet. Through this as well as many other publications it has been clearly shown that hydrogen is the real source of this defect.

Moore, Mason and Harrison(2) have given the latest scientific interpretation of fishscales. By using heavy water in place of ordinary water they revealed with the mass spectrometer that dissolved water in frits is the main source of this defect. So all the earlier papers were refuted which had overestimated the importance of hydrogen absorbed during pickling, hydrogen resulting from the milling water, hydrogen resulting from chemically bound water in clay, or from the steam in the furnace.

It is well known, that the danger of formation of fishscales rises with the increasing thickness of steel sheets when enamelled on both sides. Sieverts and collaborators(3) have stated already that the absorption of hydrogen in iron and steel depends on the quantity of hydrogen offered per

*Fig. 8c—Fishscales which penetrate the cover coat only.*

*Fig. 8d—"Shiners".*

time unit, and on the temperature, as well as on the gauge of the steel sheet.

As shown in Fig. 2 the gauge of steel sheets for covers is, up to a diameter of 240 mm., 0.75 mm. and for higher diameters, 1.0 to 1.5 mm.

Two factors may be decisive for the absence of fishscales up to a diameter of 280 mm.:

(i) the adherence of the enamel on the steel sheet and its physical structure,

(ii) the hydrogen emanating from the steel sheet after the enamelling process.

The first-mentioned factor is stronger than the other, *i.e.*, the pressure of the hydrogen emanating from the steel sheet with a gauge of 0.75 to 1.0 mm. is not sufficient to form fishscales. Covers with a diameter of 300 mm. and upwards cannot any more be called enamelled on both sides in the usual sense as here the hydrogen arising from the steel sheet can leave the special coat through the existing capillary structure.

### *" G " and " E " pans*

Neither type of pan shows a higher proportion of fishscales than 1 per cent.

The following points may help to explain the comparatively low proportion of fishscales although the steel sheets have a high gauge of 1.5 to 2.0 mm. for " G "-pans and 3.5 to 5.0 mm. for " E "-pans:

(i) The outside bottoms of the " G "-pans are covered with the above-mentioned special coating permeable for gas and the bottoms of the " E "-pans are not coated at all.

(ii) The sides of the pans which are enamelled inside and outside have a height up to 50 mm. and the sides of the " E "-pans are thinned down from 3.5 to 2.0 mm. and from 5.0 to 2.5 mm. respectively.

Already here it appears clearly that fishscales are not only dependent on the thickness of the steel sheets but also on the area of the sheet on both sides.

The rate of fishscaling on pans lies at 16 per cent when compared with the percentage of fishscales according to the height of the pots shown in Fig. 7. This comparison fits quite well.

Another hint is the earlier-mentioned observation that fishscales prefer to appear in the central zone of pots, *i.e.*, generally between 20 mm. from the bottom and from the rim. This circumstance may lead it to be supposed that the hydrogen following the way of least resistance in the above-mentioned zone escapes through the enamel-free bottom and rim. Thus it may virtually be taken

that the sides of pans with a height of 50 mm. cannot be considered as an area enamelled on both sides.

*" G "-pots*

The big difference in the appearance of fishscales between " G " and " E "-pots is striking. When examining the cause of fishscales on covers and pans, two factors were decisive, thickness of sheet, and area coated on both sides with enamel.

Fig. 2 shows for the pots here under examination a sheet gauge of 2.5 mm. up to a diameter of 260 mm. and 3.0 mm. at a diameter of 280 mm. The thickness of the sheets is reduced on both sizes, as already mentioned above, to 1.5 mm. by drawing and rolling.

Fig. 3 shows that the rim of the pot has the same thickness as the steel sheet, thus giving it a higher mechanical strength; this strengthened rim is up to 18 mm. deep.

The proportion of gauges of sides to bottoms and rims is 1 : 1.6 for " G "-pots. These differences in thickness of the material have—so it seems—no great influence on the appearance of fishscales.

The rate of fishscaling shows a yearly average of 1.0 per cent. However, sometimes a high percentage of them appears on particular orders. In production a specially severe surveillance is executed for the following points:

(*a*) examination of raw materials,
(*b*) smelting state of frits,
(*c*) control of expansion,
(*d*) fineness of enamel, specific gravity and dipping weight of enamel slip,
(*e*) firing state, and thickness of application of ground and cover coat.

As in all observed cases several orders of different dimensions passed through production and as one of them only showed fishscales in a period of several days, the conditions of production cannot be the principal cause for this defect. The steel sheet as the main source of fishscales on pots will be treated in detail in the next paragraph, together with the " E "-pots.

*" E "-pots*

As already reported above, fishscales almost exclusively crop up on the outside of pots. Their appearance may be favoured by the following possibilities:

*Tensions in both cover coats*

In the inside cover coat high compressive tensions exist as a result of the comparatively low coefficient of expansion. Compressive strength and adherence work together on the inside of pots so that the danger of fishscales is reduced.

The expansion of the outside cover coat is

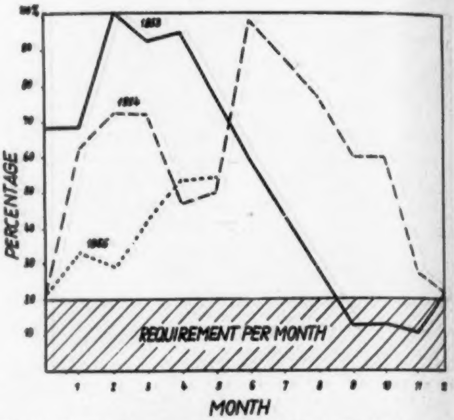



*Fig. 9—Graph showing stocks of* 3-*mm. thick steel sheets for the years* 1953, 1954, 1955.

adjusted to $300 \times 10^{-7}$. The outside finish coat is stressed by low compressive tension in the steel-enamel system. The strength of bursting increases greatly on the outside of bends when a compressive tension exists. These compressive tensions are balanced by the adherence. Thus a low pressure of gas coming out of the sheet is sufficient to form fishscales.

*Bubble structure in enamel*

The inside finish coat is interlaced with a net of fine bubbles over the whole cross-section arising from its high viscosity.

Higgins and Deringer(4) have found that a certain connexion exists between the bubble structure of enamel, and its resistance to formation of fishscales.

In the outside cover coat a bubble structure does not exist. The black finish enamel is adjusted to a low viscosity to get a dark shade colour and a high brightness. The enamel has more a glass-like structure and has a low resistance to mechanical tensions.

*Steel sheet.*

Although it has been stated earlier in this paper that once-pickled steel sheets are used, it is necessary to correct this. Until October, 1953, twice-pickled steel sheets were employed which had the nomination steel group VII according to German Industrial Standards " DIN " 1623.

Besides others, Heimsoeth and Mayer(5) have shown that the quality of steel has a decisive influence on scrap and especially on the formation of fishscales.

Besides the quality the age of steel sheets is important for enamelling. A. Dietzel and E. Wegener(6) state in their paper about sheets for

enamelling and enamellability of steel sheets, that it would be better to work with sheets stored for a longer period. During the whole period of observation it was observed again and again that "green" sheets, *i.e.*, sheets not stored long enough, showed considerable fishscaling although the physical examination was quite correct. To get a possibility of comparison between the values of Fig. 6 showing the appearance of fishscales and the period of storage of sheets, Fig. 9 shows the stock of 3-mm. sheets during the whole period of observation. The stock figures of 2.5-and 3.5-mm. sheets are similar.

In the period from November, 1953, to August, 1954, the enamelling department had to work mostly with sheets of inferior quality. The surface of the sheets showed lots of pores, scars, rolled-in scale and non-metallic inclusions. Besides, there were internal cracks and pores in the sheets some of which continued along the length of the strip. Enamelling was only possible after treatment by sandblasting. If this additional work was not executed or defects existed in the inside of the sheets, then the result was a continuous development of gas during the fusing of the ground and final enamel coats leading to pores, craters and dark spots.

Fig. 11 shows the influence of non-metallic inclusions on creation of fishscales. These inclusions are spread during hot rolling along the grain boundaries in a banded structure in the rolling direction. They have a special influence when they stay on the surface.

To prevent the processing of sheets of poor quality in regard to fishscales, all sheets were classified on receipt according to their qualities as

*Fig. 10 (above)—Inside of pot showing bad surface defects.*

*Fig. 11 (below)—Influence of non-metallic inclusions on the formation of fishscales.*

from June, 1954. The following tests were carried out:

Visual examination of surface after grinding across and along rolling direction.

Deep etching of surface and cross-section of sheet. Enamelling test for fishscaling.

Then the sheets are used according to their qualities for the production of pots, pans and covers as these are more or less resistant against fishscales.

The sheets are stored by gauge, producer and date of delivery. Every order entering production is accompanied by a card with a number which makes it possible to find out quickly the results of the abovementioned tests.

*Firing Conditions*

As stated earlier in the plant description the heat for the firing of the ware comes from the surrounding wall, the ceiling and the bottom of the furnace. The rotating core carrying the pots has no heating coils.

A great difference of temperature exists between sides and bottoms of " E "-pots. The ratio of the thickness of sides to bottoms is:

" G "-pots ... ... 1 : 1.6
" E "-pots ... ... 1 : 2.0 to 1 : 2.3

The firing experiments set out in Table I were executed under production conditions with firing period up to 5 minutes at ½-min. increments. The table clearly shows that bottom and sides of " G "-pots are nearly always in the same firing state while the sides of " E "-pots are 2 minutes ahead of the bottoms. The unavoidable result is that the sides are overfired by the time the bottoms reach the proper firing temperature.

A series of firing experiments were carried out on " E "-pots of high shape to examine the adhering layer and the state of firing of sides and bottoms.

To get more distinctive results normal ground-coat enamel was used in which the quantity of cobalt oxide was reduced to 0.1 per cent. The enamel was then tested for impact resistance by a falling weight device developed in the Max Plank Institute for Silicate Research. A falling weight of 6.0 kg. was used. The findings of these experiments were as follows:

On the bottom the bubble structure showed many compactly packed bubbles with a diameter of about 0.05 mm., few of them up to a diameter of 0.12 mm.

After impact testing, amongst 10 spots the average diameter of splintered enamel was 0.20 mm. In the centre of the spot an enamel mushroom remained, and the surrounding area showed a distinctly rough, grey steel surface. The splitting spot was nearly round and garnished with single small islands of the so-called adhering layer. The transition to the ground enamel was graduated in 3 stages.

Table I.

Firing experiments with pots of high shape of " G "- and " E "-type (ground coat):

| *Time of fusing* | *" G "-pots* | *" E "-pots* |
|---|---|---|
| 1 minute | Sides all softened, bottom partly. | The upper ⅔ of the sides show the first dark spots as softening starts. |
| 2 minutes | Sides and bottoms nearly melted. | The upper ⅔ begin to melt (first appearance of brightness). The bottom has not begun to soften. |
| 3 minutes | Sides and bottoms melted. | Sides as at 2 min. Bottoms show local softening. |
| 5 minutes | Sides and bottoms shining brightly. | Sides shining brightly. Bottoms as at 3 minutes. |

On examination of the bubble structure of the sides, the ground enamel showed the transformation to a glass structure, only spotlike residues of gas bubbles being recognizable. On the sides, lots of dark coloured round spots were visible by eye, which on microscopic observation, showed glass-like, completely bubble-free zones. Their origin may be a locally stronger formation of scale on the sheet and its solution in the enamel. The microscopic examination of enamel splinters from the sides showed numerous blood-red hematite crystals not present in the enamel on the bottoms.

The average diameter of splintered enamel after impact testing is 5.0 mm. The crater is not round but nearly rectangular. The de-coated surface is shining silvery and free of enamel or residues of the adhering layer. The transition to the ground coat enamel is immediate.

The result of the above firing experiments shows that the sides of " E "-pots are overfired. A. Dietzel and K. Meures(7) have investigated the particular firing stages and their influence on the formation of adhering layers. M. E. McHardy(8) has examined the bubble structure and its significance for the resistance of enamel against fishscaling. The results obtained in the present work confirm their findings and explain the higher rate of fishscaling on " E "-pots in particular.

An explanation of the comparable appearance of fishscales on " E "-pots in the years 1953, 1954, and 1955, shown in Fig. 6, can now be offered.

Although the quality of sheets was favourable at the beginning of 1953 (steel group VII-23 and stock of almost 3 months) the rate of fishscales increased more and more and reached 100 per cent in the month of March, 1953. The cause of this

was that from the beginning of the year till the end of March firing frames were used which made it possible to charge the furnace with nearly the double quantity of pots. The pots were placed in 2 decks in the furnace. The firing period was raised to 10 minutes, and the firing temperature remained the same. Thus the firing conditions mentioned in the last paragraph were reached and their harmful effects even intensified. In the months of April and May the firing temperature was lowered by about 50° C. using the same cover frits and large fishscales appeared (*see* Fig. 8b) due to insufficient formation of adhering layers.

The months of July and August show the lowest proportion of fishscales. This low rate was reached by really good working conditions and the use of sheets of high quality stored 5 months.

Beginning from November the production was using partly twice-pickled sheets and from December onward once-pickled sheets only. The stock was then below the monthly needs so that only " green " sheets could be used.

As already mentioned the delivered sheets were mostly of inferior quality up to August, 1954. Fig. 9 shows that, in production, 4-months-old sheets were available from the month of October onwards. Likewise a favourable influence could be observed by the classification of delivered sheets, started from June onwards.

The month of January, 1955, shows an increasing tendency to fishscaling. The stock of sheets nearly reached the monthly needs, but all the following values lie below these of 1954. It can be summarized that the proportion of fishscales on " E "-pots principally depends on the quality of sheets as well as on their age. It is regrettable that the above mentioned figures for fishscaling were somewhat influenced by the inclusion of fishscales on the handles which were not listed separately for a longer period.

### Large-scale Experiments in Pre-annealing in Controlled Atmospheres

Some practical large-scale experiments were carried out in the pre-annealing of ware in controlled atmospheres, and in the use of specially alloyed steel sheets.

In the pre-treatment of the raw pots by annealing in a reducing atmosphere the practical experiments were executed in a continuous furnace in an atmosphere of burned town's gas.

The annealed pots showed a bright and shining surface. An examination of the crystalline structure showed mostly a decarburized surface with large grains on which wetting with enamel slip was only possible after a short treatment in a hot solution of soda.

The influence of annealing in a controlled atmosphere on the formation of fishscales was investigated in two ways:

(i) By measurement of the diffusion of hydrogen by the M.P.I. method.[9]

The examination of the diffusion of hydrogen through sheet specimens treated in a controlled atmosphere showed similar results to untreated specimens alloyed with chromium, *i.e.*, the measured values were near the abscissa.

(ii) By enamelling tests.

The enamelling of pots pre-heated in a controlled atmosphere did not confirm the results of the first test as after 1 to 2 days already up to 95 per cent of fishscaling could be noted.

The cause was that the open-hearth furnace sheet had some locally rolled-in scale. The following experiments verify the assumption that these local spots of scale reduced to metallic steel. Samples of sheets were supplied with a thin layer of oxide by annealing in an oxidizing atmosphere. Half the surface was then pickled and transformed into a clean metallic surface. Then the samples were treated in a controlled atmosphere. After the enamelling the un-pickled part of the samples was full of fishscales. These experiments showed that even when pre-treating in a controlled atmosphere the first need is high quality of steel sheets.

### Large-scale Experiments with Titanium-alloyed Steel Sheets

In co-operation with a steel mill enamelling experiments were carried out with titanium-alloyed steel sheets. 7 tons of 3.0-mm. steel sheets alloyed with titanium were made into " E "-pots with high shape, which are not particularly resistant to fishscaling.

No fishscales resulted.

W. A. Deringer and A. O. Smith[10] have reported on enamelling properties of normal enamelling steel sheets, Armco sheets, as well as on steel sheets alloyed with chromium and titanium. They stated that re-boiling as well as the formation of fishscales depend on the base metal used. Steel sheets alloyed with Cr and Ti showed in contrast to the two other kinds of sheets, extraordinarily good enamelling properties. Our own experiments confirm this view.

### Summary

The output of heavy enamelled steel pots, etc., is often influenced to a great extent by the appearance of fishscales. To facilitate the interpretation of practical observations as well as the

(*continued in page* 344)

## The Incidence of Fishscales

(*continued from page* 343)

comparison of values, the programme of production and the different operations have been described.

The great difference between the incidence of fishscaling on " G "- and " E "-pots over the whole production range is especially striking. The factors which from practical observation are found to be of great influence are the gauge of sheets, the area covered on both sides by enamel, the state of tensions in the system sheet—groundcoat-cover-coat, as well as the bubble structure of the enamel.

Firing experiments with " G "- and " E "-pots showed the sides and bottoms of " G "-pots to have in all firing ranges a uniform firing state. On " E "-pots sides are 2 minutes ahead of bottoms. In using a ground enamel poor in adhering oxides the examination of the gas-structure and formation of adhering layer on " E "-pots of high shape showed distinct differences between bottoms and overfired sides. Hereby the cause could be established why especially " E "-pots show a higher rate of fishscales. From the interpretation of the comparable values of appearance of fishscales on " E "-pots in the years 1953, 54 and 55 it appears that, besides the firing stage, the main cause of this defect is the capability of the sheet to absorb hydrogen, which can be reduced by ageing as well as by quality.

The large-scale experiments showed that pre-treatment by annealing in controlled atmosphere of the raw pots as well as enamelling experiments with titanium alloyed steel sheets, again emphasized the significance of the steel sheet as base metal of enamel.

### References

(1) Hoff, H. and Klarding, J. "Connexion Between Formation of Gas and Formation of Fishscales during the Process of Enamelling" *Stahl u. Eisen*, **58**, (1938).
(2) Moore, D. G., Mason, Mary A., Harrison, W. N. *Ceramic Age* (May 1952).
(3) Sieverts, A. *Z. Physik. Chemie*, 77( 1911).
(4) Higgins, W. W., Deringer, W. A., *Journal Amer.Ceram.Soc.* 24 (1941).
(5) Heimsoeth, W. and Mayer, F. R., *Ber.d.D.K.G. and V.D.E.Fa.*, 7, 1952.
(6) Dietzel, A. and Wegener, E., *Mitteilungen d.V.D.E.Fa.* 5, 1954.
(7) Dietzel, A. and Meures, K., *Sprechsaal* **38** (1933).
(8) McHardy, M. E., *Ceramic Industry* March (1949).
(9) Dietzel A. and Stegmaier, W. *Berichte der D. K. G. and V. D. E. Fa.* 4, 1952.
(10) Deringer, W. A. and Smith, A. O. *Ceramic Industry* May 1950.

## Chromium Diffusion—Discussion

(*continued from page* 334)

chromium diffusion, and if done in a normal atmosphere the appearance would be spoilt, so that it was necessary to use a reducing or controlled atmosphere for the purpose. Mr. Samuel had to agree with that. It all depended on whether the part was required for decorative or for purely functional purposes. In very many cases heat treatment was carried out after chromium diffusion and it did not matter if the part was slightly grey in appearance, because it was not used for decorative purposes. If it was to be used for decorative purposes there had to be some method of descaling afterwards; such methods existed.

With regard to the reduction of the impact properties, if there was a very strong decarburization of a medium carbon steel the physical properties would be considerably altered, even after heat treatment, and the loss of carbon would never be recovered, but if those properties had not been very much upset the impact properties were not to any extent impaired. In some cases, with alloy steels, the fatigue strength could even be improved, although it was usually slightly less or just about the same. In the case of certain nickel alloys it had been very definitely improved.

Mr. Muir stated that Nimonics could be chromized, but that no improved results could be obtained. Mr. Samuel said that he believed that he knew that Mr. Muir had in mind. He had investigated this rather thoroughly, and in fact there was a very marked improvement, not on the ordinary 80/20 nickel-chromium alloy but on the creep-resisting types, where there was a considerable amount of precipitation hardening. In some cases the rate of oxidation was reduced to one-tenth of what it would be in normal conditions. If $SO^2$ was present or the atmosphere was slightly reducing and sulphur was present, the amount of corrosion was very much reduced and there was no occurrence of intergranular corrosion, which was one of the greatest difficulties with those alloys. That applied to stainless austenitic steels as well, which were treated in the same manner.

The last point was the diffusion of aluminium to improve the resistance to high temperatures. It was not always necessary to do that. It was easy to improve the properties at the very highest temperatures by choosing a metal which would give a coating which was stable at those temperatures. He had shown a graph with low-carbon steel which made it clear that above 900° C the material began to show rediffusion effects after a few hundred hours. On the same graph, with the high-carbon steels and certain types of alloy steels, the same effect would only begin after more than 1,000 hours. It was, therefore, often possible to select the right material when the precise conditions of use were known beforehand.

FINISHING NEWS REVIEW

# INSTITUTE OF VITREOUS ENAMELLERS

## Annual Conference to be held in Brighton

THE twenty-second annual meeting of the Institute of Vitreous Enamellers will be held at the Hotel Metropole, Brighton, on October 4 and 5 this year. The programme, which is set out in detail below, includes the formal annual general meeting of the Institute, after which a number of technical sessions have been organized. The proceedings culminate in the annual banquet to be held at the Winter Gardens, at which guests will be received by the newly inducted president of the Institute, Mr. C. R. WHEELER and Mrs. WHEELER.

Programmes and application forms for participation in this Conference are obtainable from Mr. J. D. GARDOM, Secretary, Institute of Vitreous Enamellers, Ripley, Nr. Derby.

### Programme

All technical sessions are held in the Hotel Metropole.

**Thursday, October 4**

10.00 a.m.— Annual General Meeting—*Octagon Room*

11.30 a.m.—*1st Technical Session* "Enamel as a Finish" by T. J. MCARTHUR—*Octagon Room*

1.00 p.m. — Luncheon — *Centre Room*

2.30 p.m.—*2nd Technical Session* Symposium on Mechanical Handling—*Octagon Room*

(*a*) "Pickling and Pre-Treatment" by J. STACK

(*b*) "Enamel Application" by W. B. NOON

(*c*) "Drying and Fusing" by T. MACPHERSON LEES

During the afternoon a visit has been arranged for ladies to Parnham Park, taking tea at the Manor House Hotel, Storrington. Departure is at 2.30 from the Hotel Metropole.

**Friday, October 5**

10.00 a.m.—Inauguration of C. R. WHEELER, C.B.E., as President, followed by Presidential Address—*Octagon Room*

11.15 a.m.—*3rd Technical Session* "Abrasion Resistance of Enamels" by B. K. NIKLEWSKI, M.Ph., M.S., D.Sc.Tech. —*Octagon Room*

1.00 p.m.—Luncheon — *Centre Room*

2.30 p.m.—*4th Technical Session* "An Eye to Colour" by E. W. B. DUNNING — *Octagon Room*

3.30 p.m.—*Discussion Session* "Current Mill Room Practice" by S. H. RYDER, B.Sc., A.R.I.C., A.I.M.—*Octagon Room*

4.15 p.m.—*Film Show* "Titanium Pigment Story" —*Octagon Room*

7.30 p.m.—Reception by President and Mrs. C. R. WHEELER and Chairman and Mrs. W. THOMAS—*Winter Gardens*

8.00 p.m.—Annual Banquet — *Clarence Room*

10.00 p.m. until 1.00 a.m.— Dancing—*Winter Gardens*

## WELL-KNOWN PLATING FIRMS AMALGAMATE

The amalgamation has been announced between the two well-known and old-established metal finishing firms of B. J. Round and Sons Ltd. and James Evans and Sons.

B. J. Round and Sons Ltd. have acquired a controlling interest in the firm of J. Evans and Sons, which will become a limited company under the title of J. Evans and Sons (Gilders) Ltd. and will continue to operate in their present premises with their present experienced staff, specializing in the polishing, lapping, gilding and rhodium plating of high-class gold, silver and platinum jewellery.

Mr. A. B. Denton, who entered into partnership with Mr. E. J. Evans in 1946 is retiring, but Mr. Evans remains on the Board, of whom the other members are Mr. A. J. Round (chairman), Mr. J. Warwick Round (managing), Mr. Geoffrey Round and Mr. H. G. Mitchell (secretary).

It is interesting to note in connexion with this announcement that Mr. James Evans, the founder of the Evans firm, served his apprenticeship with the late Mr. B. J. Round, the founder of the Round firm, and Mr. J. W. Round as the latters great-grandson, represents the fourth generation of the family in the company, which was established in 1864.

## DESIGN DISPLAY

The importance of paying adequate attention to certain fundamental design criteria as a prerequisite to obtaining a sound and economic plated finish is not even today sufficiently widely recognised. It is to be hoped that valuable guidance in this connexion will be obtained from a special display to show the work done by the Council of Industrial Design's record of designers which is to be held at the Design Centre, Haymarket, London, S W 1, from September, 10-.29. It is hoped that the Exhibition will encourage business concerns to seek advice from the Record on their design problems.


# EXPANSION MOVE BY
# New Crawley Factory for

ANOTHER milestone in the progress of a virile metal finishing organization was passed when Metachemical Processes Ltd. last month occupied a new factory on the new trading estate at Crawley. Since the company was formed in 1948 as largely a single-handed venture by its present managing director, Mr. H. D. Hughes, it has succeeded in making its mark on more than one occasion on the technology and practice of electro-deposition in this country.

*A part of one of the laboratories at the new works of Metachemical Processes Ltd. in which research and development work is carried out on electroplating and electrochemical processes.*

*A problem posed by a customer is discussed by Mr. H. D. Hughes, A.I.M., managing director of the company, and Mr. R. W. Lewis, M.B.E., the technical director. Particular emphasis is laid by the company on full consultation with customers at all stages of the production of components destined for ultimate plating.*

Its origin stemmed largely from the conviction held by Mr. Hughes when he was acting as an electroplating consultant that a very great deal of electroplating carried out in this country was of inferior quality, a view which is undoubtedly shared by many reputable plating companies. Foreseeing the need for an organization which would offer to manufacturers a guaranteed quality of finish, Mr. Hughes, with the assistance of his wife, launched the company in premises made available to him by an engineering company in Acton. In the course of time the whole factory building was acquired and a number of substantial plating contracts had been obtained.

One of the keystones of the successful operation of the company has been the insistence on co-operation with customers to ensure that components sent for plating are suitably designed and of adequate material quality for the deposition of a high quality and durable finish. Much of the present high cost and indifferent quality of some plated finishes can be directly attributed to the fact that many articles sent out for plating are of such a design as to render the plating process difficult or virtually impossible or manufactured from a material whose surface finish does not lend itself readily to high quality plating. By entering into consulation with manufacturers right from the design stage of a component, Mr. Hughes has made it possible to offer a very effective plating service.

A recent extension of the activities of the company has been the acquisition of a share in the world rights of the Dalic process of electrodeposition. This process, which as is generally well-known, provides a means for the local application of an electrodeposited coating at high speeds of deposition and to a closely controllable thickness, is finding increasing application in a wide range of industries. The company will either undertake plating

# PLATING SPECIALISTS
## Metachemical Processes Ltd.

work by the Dalic process for customers or will supply the necessary equipment and solutions for the operation of the process in the customer's own works.

In association with the French company which developed the process, Metachemical Processes Ltd. have formed a company in Canada with rights in the U.S.A. and are planning extensions to other parts of the world.

The move to Crawley has enabled the company to set up one of the most effective industrial laboratories in this country for research into electrodeposition and other electrochemical phenomena. One section of this works is devoted to the manufacture of equipment and solutions for the Dalic process, while a laboratory has been set aside for demonstration and development work in connexion with the process. Facilities are offered for the training of operatives in the use of the Dalic equipment and the technique of operating the process can be rapidly acquired by any operative of average skill. All plating solutions are supplied ready for use and service in the form of the provision of special anodes, etc., is available when required. Detailed advice on the application of the Dalic process to particular problems can be supplied by the company at short notice.

The new laboratory has enhanced the facilities available to the company for research and development of new processes and techniques of electrodeposition and in the more general field of electrochemistry.

The general plating production department is equipped for the deposition of nickel, chromium, hard chromium, cadmium, zinc, copper, tin/zinc, heavy copper and a number of precious metals, including gold, silver and rhodium.

Another field in which the company has carried out intensive development work is in the plating of plastics, and methods have been evolved for the deposition of a wide range of metals onto various plastic metals for both

deposition of a wide range of metals on to various plastic materials for both

(*Continued on page* 348)

*Part of another laboratory in the new building which is devoted to development work in connexion with applications of the Dalic brush plating process.*

*A view of the laboratory where the special solutions are made up for use in conjunction with Dalic brush plating equipment.*


## TECHNICAL AND INDUSTRIAL APPOINTMENTS

The board of **Metachemical Processes Ltd.** has been joined by Mr. R. P. Richardson, formerly a director of **Burndept Ltd.** Mr. Richardson will assist in the promotion of new projects in electrodeposition and electrochemistry in the laboratories of the company in their new factory premises at Crawley. The company are well known as the agents in this country for the Dalic process of rapid local plating for the recovery of worn or over-machined components.

* * *

Mr. R. McKinnon Wood, chairman of **Griffin and George Ltd.**, laboratory furnishers, has been appointed vice-chairman of the committee, under the chairmanship of Professor Willis Jackson, which will advise the Government on the recruiting and training of technical college teachers.

* * *

On August 27 Dr. H. W. Melville took up his appointment as Secretary of the **Department of Scientific and Industrial Research.** Dr. Melville was previously Mason Professor of Chemistry at Birmingham University.

### CHANGE OF NAME

Durtnall and Hipwell Ltd., Riverside Estate, The Causeway, Staines, Middlesex, have changed their name to **D. and H. Metal Treatments Ltd.**

This company continues to operate, on the contract basis, the sodium hydride cleansing plant at the Staines works.

### PRICE INCREASE IN BORON PRODUCTS

Notification has been received from **Borax Consolidated Ltd.** and **Borax and Chemicals Ltd.** that there will be an increase, effective from October 1, 1956, of £1 per ton in the price of borax and boric acid. This increase has been necessitated by a further increase in ocean freight and transport costs.

Until the effective date of the price increase normal supplies will be available to customers at current prices.

# CHEMICALS FROM PETROLEUM

**Expansion Programme Announced by Monsanto**

IMPORTANT developments in the manufacture in Great Britain of new industrial chemicals from petroleum have been announced by Monsanto Chemicals Ltd.

The company plans to spend some £8½m. on the first stage of a long term expansion programme. As was indicated in the company's report for the year 1955 a new factory will be constructed on a 100-acre site alongside the Fawley, Hampshire, refinery of the Esso Petroleum Co. Ltd. from which Monsanto will draw feedstock for conversion into a wide variety of raw materials for use in the plastics, textile, rubber, paint, paper and other manufacturing industries.

The first plant to be erected will be for the manufacture of 10,000 tons of polyethylene a year. Survey work is being carried out on the site, construction will begin shortly and production is scheduled to start in 1958.

Polyethylene, one of the most versatile of plastics, is being used increasingly in many types of packaging and for cable coatings, seamless tubing and thousands of articles for industrial and household use.

The next products in the company's programme will be copolymers of acrylonitrile, butadiene and other monomers. The copolymers have a wide range of uses in the rubber, paint, plastics, paper and other industries.

Following this a major plant is to be constructed for the manufacture of acrylonitrile, an important chemical not yet made in this country. Acrylonitrile is an essential raw material for synthetic polymers and synthetic fibres used in the production of high quality clothing materials and other textile fabrics.

This expansion programme is a continuance of Monsanto's established policy of maintaining and developing indigenous sources of basic raw materials for use by exporting industries. It is hoped that the new products to be manufactured will make a considerable contribution to Britain's export trade, not only in bulk raw materials but indirectly in finished goods.

## Expansion Move by Plating Firm

(*continued from page* 347)

decorative and engineering purposes. In some cases the substitution of electroplated plastic components for the more commonly encountered plated metal component has shown substantial savings in total cost.

Although the main activities of the company are now based on the Crawley factory, the works previously occupied at Acton has been retained as it is anticipated that the additional space will shortly be required to accommodate further projects which are present at the planning stage.

*A representative collection of components fabricated from various plastic materials and electroplated by special techniques evolved by Metachemical Processes Ltd. In many cases such plastic components show cost savings over more orthodox metal products.*

# PLATING SHOP EFFLUENTS

## Birmingham Corporation to Impose Charges

AT A meeting held on August 22 between members of the Metal Finishing Association and the Birmingham City Council, local industrialists were told that it was largely their fault that the Birmingham Corporation had decided to impose a charge for the disposal of waste water from their premises.

Mr. S. J. Asher, Birmingham chief engineer of sewers and rivers, said that industry's carelessness with wastes, and ever-increasing demand for water had forced the Corporation to do something. The Corporation has been entitled to impose such a charge by the Public Health (Drainage of Trade Premises) Act of 1937, but has not previously done so. Neither has it strictly enforced other provisions of the Act for the regulation of the discharge of certain types of effluent.

"No local authority has ever been expected to remove and dispose of trade wastes" Mr. Asher said. "In Birmingham we have, in fact, always provided this service free of charge. We have had to change our ideas on this because of the enormous increase in trade waste. It has doubled since 1948. It is having almost devastating effect on sewage works all over the country".

In addition to imposing the charge, the Birmingham Corporation is to define acceptable standards for effluent, but so far no decision has yet been reached on what the charge or the standards will be.

# PRINTING and PACKAGING EXHIBITION

SOME of the latest developments in printing and packaging research will be shown at an Exhibition to be staged by The Printing Packaging and Allied Trades Research Association at Management House, 8 Hill Street, London, W.1, on October 23 and 24. On October 23 the Exhibition will be open from 2.30 to 9 p.m. and October 24 from 11 a.m. to 5.30 p.m. Admission will be free and the exhibition will be open to anyone interested in the printing and packaging industries.

The Exhibition will cover the Association's main activities of research, answering technical enquiries and providing an information and advisory service. It will be divided into three sections, printing, packaging and information. Among the printing exhibits will be included the I.S.C.C. colour aptitude test, which has been described in an earlier issue of this Journal.

One of the main packaging exhibits will be the equipment at present being used to measure the frequency and intensity of drops in transit. In the Information Section will be featured an exhibit showing how the Association can provide information on the very latest printing and packaging materials and processes. A selection of literature published by the Association and a range of books from the Library will be displayed.

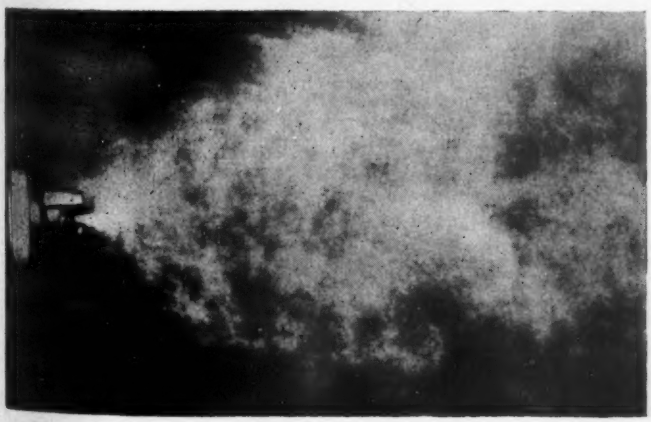

# GROWING USE OF ENAMEL IN U.S.A.

ACCORDING to a report issued by the Porcelain Enamel Institute of America, the total dollar sales of all porcelain enamel products going into end products, are expected to show an increase of 6 to 7 per cent. over those of last year. The report states that the three major users of vitreous enamel, the appliance, building materials, and industrial equipment industries, are expecting a 6 per cent. increase in total sales of enamelled products.

Household appliance manufacturers who account for more than 50 per cent. of vitreous enamel usage would expand their output by 4 per cent., and it is significant that one of the leading frit manufacturers has claimed as a result of making a number of consumer surveys that there is a 5 to 3 consumer preference for vitreous enamel exteriors on such domestic equipment as refrigerators and washing machines.

The building materials industry, which includes enamelled architectural panels, plumbing fixtures, signs and hot water tanks, has shown the largest increase in the use of vitreous enamel, and anticipates an increase of as much as 20 per cent. this year.

# ATOMIZATION BY SPRAY GUN



This photograph shows what actually takes place at the nozzle of a spray gun when it is operating at full speed.

This is a 5 microsecond (5 millionths of a second) exposure and is one of a series taken recently by Alfred Bullows and Sons Ltd., in their development section. It provides an example of the lengths to which it is necessary to go to obtain precise information on the behaviour of fluids when being atomized by compressed air.

The purpose of this series of photographs was to study (*a*) the way in which formulation of spray is produced in relation to the nozzle tip; (*b*) fluid distribution and particle size at varying pressures and (*c*) variation of both (*a*) and (*b*) for different sized nozzles.

The results are tabulated and used in the design of new nozzles and to obtain improved performance on existing equipment.


## Meetings of the Month

September 19

**Incorporated Plant Engineers (Kent Branch).** "The Corrosion of Iron and Steel and Remedial Measures", by F. S. Bricknell, Jenolite Ltd., at the Kings Head Hotel, High Street, Rochester, at 7 p.m.

September 20

**Institute of Industrial Supervisors (London South-east Section).** "Industrial and Domestic Finishes", members of the staff of Jenson and Nicholson Ltd. (Robbialac Paints), will discuss and demonstrate these products at the Woolwich Polytechnic at 7.30 p.m.

September 28

**Institute of Metal Finishing (Sheffield and North-east Branch)** "Zinc Plating", by D. N. Layton, Ph.D., M.Sc., A.R.C.S., D.I.C., A.Inst.P., at the Fitzwilliam Room, Grand Hotel, Sheffield, at 7 p.m.

October 2

**Incorporated Plant Engineers (London Branch).** "The Treatment and Disposal of Industrial Effluent", by J. Lakin, chief chemical engineer, William E. Farrer Ltd., at the Royal Society of Arts, John Adam Street, Adelphi, London, W.C.2, at 7 p.m.

October 3

**Institute of Metal Finishing (Scottish Branch).** Chairman's address by W. Watson, D.Sc., at the Institution of Engineers and Shipbuilders in Scotland, 39 Elmbank Crescent, Glasgow, at 7.30 p.m.

October 4

**Institute of Metal Finishing (Organic Finishing Group).** "The Evaluation of a Variety of Finishes on Electro-zinc Plate", by P. Costelloe A joint meeting with the North-west Branch at the Engineer's Club, Albert Square, Manchester, at 7.30 p.m.

October 8

**Incorporated Plant Engineers (Dundee Branch).** "Silicones", film and lecture by a representative of Midland Silicones Ltd., at the Mathers Hotel, Dundee, at 7.30 p.m.

October 9

**Incorporated Plant Engineers (Manchester Branch).** "Industrial Drying", by R. R. Clegg, at the Engineer's Club, Albert Square, Manchester, at 7.15 p.m.

October 18

**Incorporated Plant Engineers (Blackburn Branch).** "Steam for Process", by L. G. Northcroft, O.B.E., B.Sc.(Eng), M.I.Mech.E., M.I.H.V.E., F.I.Plant.E., at the Golden Lion Hotel, Blackburn, at 7.30 p.m.

# TRADE and TECHNICAL PUBLICATIONS

**Mond Magazine:** Another newcomer in the field of commercial periodicals is a new magazine published by The Mond Nickel Co. Ltd., Thames House, Millbank, London, S.W.1. For many years the Nickel Bulletin published by the company has provided a monthly summary of the world literature on nickel usage, and this publication will not in any way be affected by the appearance of the new magazine. The aim of the new publication is to provide interesting illustrated articles and notes on subjects related to all the products of the company. The first issue ranges widely from equipment for the production of antibiotics to stained glass windows and earth moving equipment.

The effective use of colour renders this magazine even more attractive, and further issues which are to be published periodically will be awaited with interest.

* * *

**Pre-treatment Convention:** A report of an international convention on metal pre-treatment organized by the Paint Division of Imperial Chemical Industries Ltd., under the auspices of the American Chemical Paint Co., appears in the June issue of I.C.I. *Pretreatment News.* The convention provided an opportunity for delegates, who were representative of eleven European countries, Australia and the U.S.A., to exchange information on current practice, trends and developments in metal processing. In the course of the convention delegates visited a number of works where they were able to view the company's pre-treatment plants in operation.

* * *

**Enamelled Aluminium:** The September issue of *Aluminium News,* published by Aluminium Union Ltd., includes an interesting review of the many uses now being found, principally in the U.S.A., for aluminium coated with vitreous enamel. After briefly describing the coating process, the article quotes the results of a number of performance tests. One of the advantages claimed for the material, is the ease with which it can be fabricated. Enamelled aluminium can be sheared, drilled, sawed, or punched without spalling of the coating and can be welded on the reverse side without damage to the enamel.

Although only recently on the market in the U.S.A. (and so far not available at all in the U.K.), the material is already finding acceptance for a wide range of applications. The Porcelain Enamel Institute of the U.S.A. estimates that the demand for enamel frits for use on aluminium will by 1970 have reached an annual total of 100,000 tons.

* * *

**Rust and Corrosion Preventives:** Detailed comments on factors influencing the selection of rust preventives are included in *Industrial Technical Bulletin* No. 9, issued by the Mobile Oil Co. Ltd., Westminster, London, S.W.1. After describing the conditions which give rise to rusting and other forms of corrosion and methods of combating them, the publication lists a number of the company's products designed for temporary rust prevention.

* * *

**Epoxide Resins at Sea:** The corrosion resistant properties of coating materials based on epoxy resins are becoming well known and an interesting application of one of these materials is referred to in the current *Bulletin* No. 163, published by Aero Research Ltd., Duxford, Cambridge. In this instance Araldite 121N was used to restore the surface of the rudder of the "Queen Elizabeth", which had been pitted by the erosive action of sea water. The surface of the rudder was cleaned by shot blasting and the Araldite mixed with a suitable hardener was applied over the eroded areas.

Although the success of this operation, which was carried out over a year ago cannot be established for some time yet, it shows such promise that the trial has been extended to another vessel.

* * *

**Car Body Protection:** Tribute to the deserved reputation for dependability earned by the Austin Motor Co. Ltd., is paid in the current issue of the *Bonderizer*, published by The Pyrene Co. Ltd., Metal Finishing Division, Great West Road, Brentford, Middlesex. The Austin Co. are among the oldest users of Pyrene Metal finishing processes in this country, having installed a single plant operating the original Parkerizing "A" process in 1930.

Today in all, six Parkerizing plants are operated in the Austin works with a total capacity over 2,800 gallons, apart from two Parco-Lubrite plants, a Roto-dip Bonderizing installation for body shells and a Pylumin plant for the pre-treatment of light alloy components.

# Latest Developments in PLANT, PROCESSES AND EQUIPMENT

## Metal Cleaning Process

INTRODUCED to the English market for the first time is a new process for the complete cleaning of metal parts in one operation. Known as the Pertrinol metal cleaning process, it not only removes oils, fats and grease but also cleans off insoluble soil such as carborundum, tripoli and chalk, *i.e.*, the residue of polishing and buffing compositions.

The process was developed by the German firm, Wacker-Chemie, who have had 30 years' experience in the design and manufacture of degreasing plant. The sole licensees in the United Kingdom for the plant, of which there is a complete range, and for the additive necessary for the process, are Roto-Finish Ltd., Mark Road, Hemel Hempstead, Herts.

The equipment used is similar in principle to that of a liquor/vapour solvent degreaser, but incorporates three separate compartments. The main cleaning action is achieved in the first compartment which usually contains boiling trichlorethylene. In the past it has been found that trichlorethylene would rapidly dissolve oils, fats and grease, but it often failed to remove the fine insoluble particles from polishing and buffing compositions. Under the new process this soil is removed by adding fine plastic particles (which can be either globular or fibrous) to the trichlorethylene. This plastic material is called Pertrinol and does not disintegrate in the hot solvent but becomes slightly swollen and softened. When 5 per cent. by weight of Pertrinol is added to boiling trichlorethylene the Pertrinol particles circulate automatically, and, as soon as the wax or grease has been dissolved by the solvent, scrub the surface of the component, rapidly removing all traces of dirt.

The Pertrinol particles are so fine that they penetrate into crevices, threads, etc., achieving a degree of cleanliness that previously has only been possible by additional hand scrubbing.

After immersion in the first compartment the metal parts, contained either in a barrel or a perforated basket, are transferred to a second compartment containing cold solvent. This serves to wash off any remnants or Pertrinol particles which may have been carried over, and to cool the metal parts so they can be given a final vapour degreasing in the third compartment. In order to maintain a high degree of cleanliness, provision is made in the Pertrinol plant for continuous circulation distillation and the return of clean solvent to the cleaning apparatus.

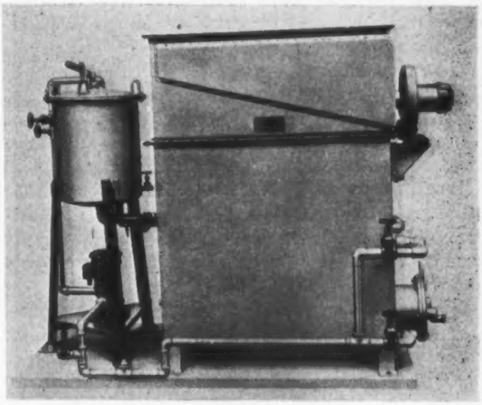


*Fig 1. Metal-cleaning plant*

## Cloth and Sisal Multi-tooth Buffs

TWO new sectional types of buffing wheels have been announced by the Schaffner Manufacturing Co. Inc., Schaffner Center, Pittsburgh 2, Pa., U.S.A.

Type Number 1: Cloth and sisal multi-tooth buffs are designed for heavy and medium metal-finishing processes for fast thorough cutting and colour of intricate contoured metal surfaces. They are claimed to cut and colour metal in a single operation. Both types of buffs utilize double-folded tufts to provide maximum cutting surface and hold buffing compound at the leading edges and on the buff's circumference. Teeth are staggered in a double row around the buff to prevent streaking. This also makes the buff self-ventilating for cooler operation.

A steel centre, composed of two steel discs, provides support for each buff. The steel clamps around the circumference of the discs to hold the buff in place. Added strength is accomplished by heavy-duty stitching around the buff's inner circumference. The steel discs are multiple-spot-welded together. A number of venting holes in the steel centre assures free circulation of air from the centre of the buff to its periphery.

The buffs are made of top-grade sisal cloth, covered with bias-cut cotton cloth. The four rows of stitching of each tooth, plus its double-fold construction are claimed to keep the cloth from fraying, and to increase buff life. This buff is suitable for hard and heavy cutting of steel and stainless steel.

Type Number 2: All-cloth multi-tooth are made

of top grade 86/93 bias-cut buffing cloth, with each tooth stitched twice to assure greater flexibility of the buff.

Both buffs are available in diameter ranges from 10 to 24 in.

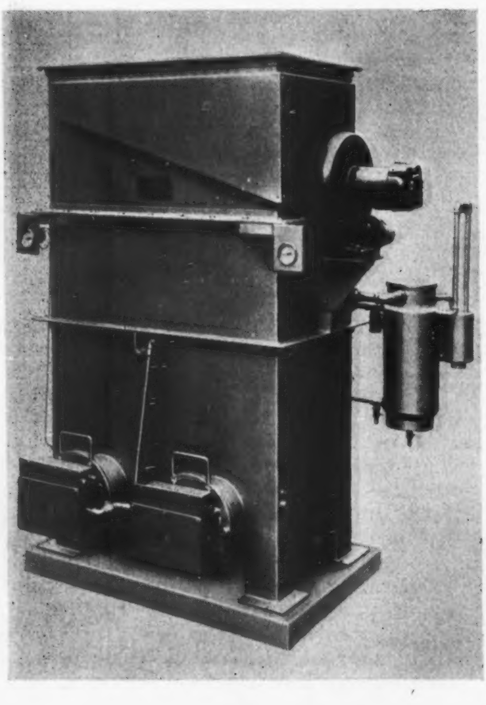
### Metal Dryer

A NEW method for drying metal parts rapidly and without trace of water staining has been developed by the German company Wacker-Chemie.

The new method, known as "ASL", consists of immersing the parts to be dried in boiling perchlorethylene to which has been added a special agent. This agent has the property of reducing the adherence of water to the surface of metal and of promoting the transference of heat from perchlorethylene to water. The result is that the water evaporates much more rapidly than in pure perchlorethylene and does not tend to form an emulsion. Due to the speed of evaporation all the impurities in the water are removed simultaneously from the surfaces of the metal parts leaving them stain free. Only minute quantities of the additive "ASL" are required, a ratio of 0·1 per cent. by weight of "ASL" to perchlorethylene being satisfactory.

In addition to the "ASL" agent, "ASL" metal-drying plant is being marketed. This plant incorporates a water separator which ensures that the drying process is maintained without risk of deterioration due to water contamination of the bath.

*Fig. 2. Metal-drying plant*



Roto-Finish Ltd., Mark Road, Hemel Hempstead, Hertfordshire, are the sole United Kingdom suppliers of "ASL" metal drying plant and "ASL" additive.

### Stoving Finish

ANNOUNCED by Wm. Harland and Son Ltd., Merton, London, S.W.19, is an industrial stoving finish which has a deep-textured pattern claimed to hide imperfections with a single coat on all but the roughest surfaces.

It provides an economical method of producing a high-gloss finish on rough castings, etc., as laborious filling and rubbing operations may be omitted.

This Duo-Tone finish can be applied by using standard spraying equipment and good results can be obtained on vertical surfaces. It also produces a hard-wearing, mar-proof film of good gloss and heat resistance. Twelve shades are available, but these can, if necessary, be adjusted to suit most individual requirements.

Harland's High Relief Duo-Tone finish is supplied at a viscosity of 100 secs. (No. 4 Ford Cup) at 20° C and for all normal work it should be applied by spray without thinning. If a finer pattern is required, the material may be thinned with not more than 10 per cent. special thinners, but this should not be done if vertical surfaces are to be sprayed. With normal spraying equipment, one full coat should be applied using an air pressure of approximately 50 lb. per sq. in. The material should not be spattered on and an excessive weight of film should be avoided on vertical surfaces. Following this a flash-off period of approximately ten minutes at room temperature should be allowed. The time necessary for stoving is thirty minutes at 250° F in a convection oven. Infra-red stoving may also be employed, but the schedule will depend upon the weight of metal involved.